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PRESSURE BAKED GRAPHITE MATERIALS

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AF Materials Laboratory

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Project No. 7350, Task No. 735002

GREAT LAKES RESEARCH CORP.
ELIZABETHTON, TENN.

(Prepared under Contract No. AF 33 (657)-11738 by the Great Lakes Research Corp., Elizabethton, Tennessee; Glen Stecker, author).

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FOREWORD

This report was prepared by the Great Lakes Research Corporation, Elizabethton, Tennessee, under USAF Contract No. AF33(657)-11738. The contract was initiated under Project No. 7350 "Refractory Inorganic Non-Metallic Materials", Task No. 735002 "Refractory Inorganic Non-Metallic Materials: Graphite." The work was administered under the direction of the AF Materials Laboratory, Research and Technology Division, Wright-Patterson AFB, Ohio, with Mr. C. A. Pratt, Jr. as the Project Engineer.

This report covers work conducted from July, 1963 to June, 1964.

The program was under the direction of Mr. A. R. Novy, Associate Director of Research. The author wishes to acknowledge helpful suggestions by Dr. F. L. Shea, Jr., Director of Research, help in conducting the program by Messrs R. Hund and K. H. Sia, and preparation of photomicrographs by Mr. H. C. Fritz.

ABSTRACT

The objective of the program was to investigate the isostatic pressure baking process as a means for fabricating improved graphites.

Using a standard mixture of graphite flour, thermal furnace black and coal tar pitch, the optimum process conditions within the capability of the apparatus used were determined. Graphite density of 1.91 g/cc, flexural strength of 3000 psi, and compressive strength of 9000 psi was obtained.

Other aggregates and binders were screened, using the above optimum process conditions. An isotropic carbon aggregate, with thermal furnace black and coal tar pitch, resulted in a graphite having a density of 1.95 g/cc, flexural strength of 6400 psi, and compressive strength of 14,000 psi. Graphite properties were essentially isotropic.

Recommendations to increase size, temperature, and pressure capabilities, and to investigate more thoroughly certain process variables were made.

This technical documentary report has been reviewed and is approved.

W. G. RAMKE
Chief, Ceramics and Graphite Branch
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1. INTRODUCTION

Graphites having very high densities are commercially available, but other associated properties are frequently inadequate for some aerospace applications. For example, molded natural graphites have very low strengths. Conventional synthetic graphites densified by multiple impregnation suffer from lack of internal and piece-to-piece uniformity. Conventional graphites densified by reworking at graphitizing temperatures result in pieces having either highly anisotropic properties or heterogeneous internal anisotropy. Pyrolytic graphites are extremely anisotropic and are difficult to produce in adequate thicknesses.

The synthetic graphite article of commercial importance is manufactured by forming a mixture of a carbonaceous aggregate and a thermoplastic carbonaceous binder (usually coal tar pitch) into a body having a useful shape. The body is then baked to achieve a rigid, infusible condition by heating to a temperature of about 750° to 1000°C and graphitized by heating to a temperature of about 2400° to 3000°C.

It is the baking process with which we are primarily concerned in this discussion. The baking of pitch-bonded bodies is generally conducted at a relatively slow rate of temperature increase, with the bodies imbedded in and supported by a granular packing medium, frequently a mixture of coke and sand.

Coal tar pitch is a complex mixture of relatively high molecular weight organic compounds, chiefly aromatic hydrocarbons. As the temperature of a pitch-bonded body is gradually increased, the viscosity of the binder phase at first decreases, then gradually increases due to distillation of thermally stable volatile constituents, and polymerization and pyrolysis (thermal cracking) of the less volatile, more reactive constituents. After baking, about 60% to 75% of the original coal tar pitch remains as carbon and very high molecular weights hydrocarbons, which mixture in combination with the carbonaceous aggregate forms the hard, strong "amorphous" carbon intermediate in the graphite manufacturing process.

The granular packing medium generally employed in baking serves to support the body so as to prevent distortion during the period of low viscosity, and also to provide a scavenger of oxygen so as to maintain a neutral or reducing atmosphere surrounding the body.

The rate of temperature increase which can be employed safely during a conventional bake at atmospheric pressure is a function of the size and permeability of the body. If the upheat rate is too fast, ebullition of the liquid pitch may occur,

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creating large void spaces and escape fissures in the body. While the viscosity of the pitch remains low, it is possible that surface tension, in combination with mild forces exerted by the weight of the packing medium, will act to decrease the porosity of the body. However, at some undetermined point, the body becomes sufficiently rigid to resist such forces effectively.

Since the rate at which volatile constituents vaporize is dependent on the rate of heat input, this rate is usually kept low to prevent the generation of disruptive vapor pressures within the body. In conventional baking, upheat rates through the temperature range 200° to 500°C rarely exceed 150° to 200°C per day. For bodies having very large cross-sections, the upheat rate may be as low as 10° to 20° per day.

Baking under unidirectional mechanical pressure has been used to permit a much faster upheat rate, and also to increase the density of the product by compression while still in the plastic range. This process has several limitations, not the least of which is a tendency for the mechanical pressure to exert destructive forces when the body shrinks away from the mold walls, and is unsupported in the other two dimensions. Also, anisotropy of physical properties is increased.

Baking while the body is subjected to an elevated pressure exerted by an inert, or indifferent, gas has also been shown to result in a slightly higher product density, presumably due to an increased coke yield from the binder phase.

In preliminary studies at the Morton Grove laboratories of the Great Lakes Carbon Corporation an isostatic pressure baking process was devised which permitted the simultaneous application of controlled gas pressure and controlled isostatic mechanical pressure to a preformed body during baking. Several sound specimens were obtained, which after graphitization at atmospheric pressure had an apparent density of 1.92 g/cc (grams per cubic centimeter) and a permeability to helium of 5×10^{-3} cm^2/sec (square centimeters per second). Strength data were not obtained.

The present program is an extension of the preliminary studies, with an increase in the size of the specimens, and a change in the method of preforming.

The equipment and facilities were provided by the Great Lakes Research Corporation.

2. EQUIPMENT AND PROCEDURE

Briefly, the IPB (isostatic pressure baking) process consists of rapidly baking a preformed mixture of a carbonaceous aggregate and a thermoplastic carbonaceous binder under controlled gas pressure, with a controlled isostatic mechanical pressure superimposed on the preformed specimen. The gas pressure on the specimen is controlled through a separate connection to an impermeable deformable container surrounding the specimen and packing medium. The isostatic mechanical pressure is applied by means of a higher pressure external to the deformable container. Generally, the internal gas pressure is released at a controlled rate after the desired process temperature is reached, and the maximum differential pressure is maintained at that temperature for a period of several hours.

Figure 1 is a schematic diagram of the IPB equipment used in the performance of this contract. The major items of equipment had been used previously in the preliminary studies at Morton Grove, Illinois. Additional instruments, materials for a plank and sand safety enclosure, and materials for a new box-type electric furnace were purchased by GLRC (the Great Lakes Research Corporation). Labor for installation of the equipment was covered by the contract.

The instrument panel (except for the temperature recorder) is shown in Figure 2. Figure 3 is a somewhat distorted wide-angle photograph (taken from inside the safety enclosure) of the furnace, pressure vessels, and condensers.

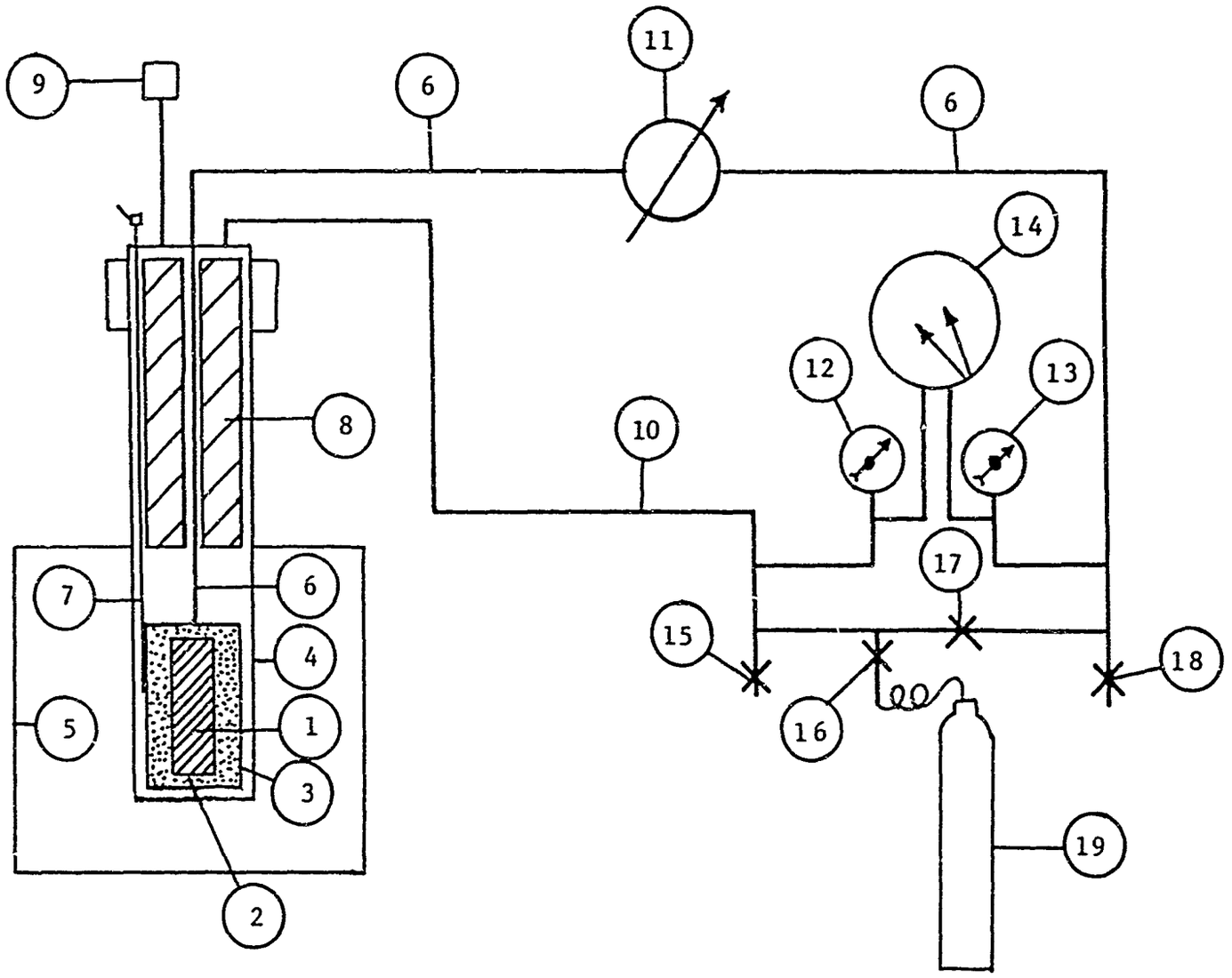
The equipment consists of the following:

(1) Two stainless steel pressure vessels (ca. 5 1/4" I.D.) designed for 2200 psig internal pressure at 593°C (1100°F), with appropriate thermocouple and pressure connections;

(2) Two water cooled condensers designed for 3000 psig internal pressure at room temperature;

(3) One electrically heated furnace to receive the pressure vessels;

(4) Fully annealed copper tubing, 4.0 in. O.D. x 0.047 in. wall thickness and 4.5 in. O.D. x 0.042 in. wall thickness, and brass discs to form end closures for the deformable containers;



1. Preformed Specimen
2. Granular Packing
3. Deformable Container
4. Pressure Vessel
5. Furnace
6. Internal Pressure Line
7. Thermocouple Well
8. Thermal Insulation
9. Safety Relief Valve
10. External Pressure Line
11. Condenser
12. External Pressure Gauge
13. Internal Pressure Gauge
14. Pressure Recorder
15. External Vent Valve
16. Pressure Supply Valve
17. Crossover Valve
18. Internal Vent Valve
19. Gas Pressure Supply

Figure 1. Schematic Diagram of IPB Apparatus

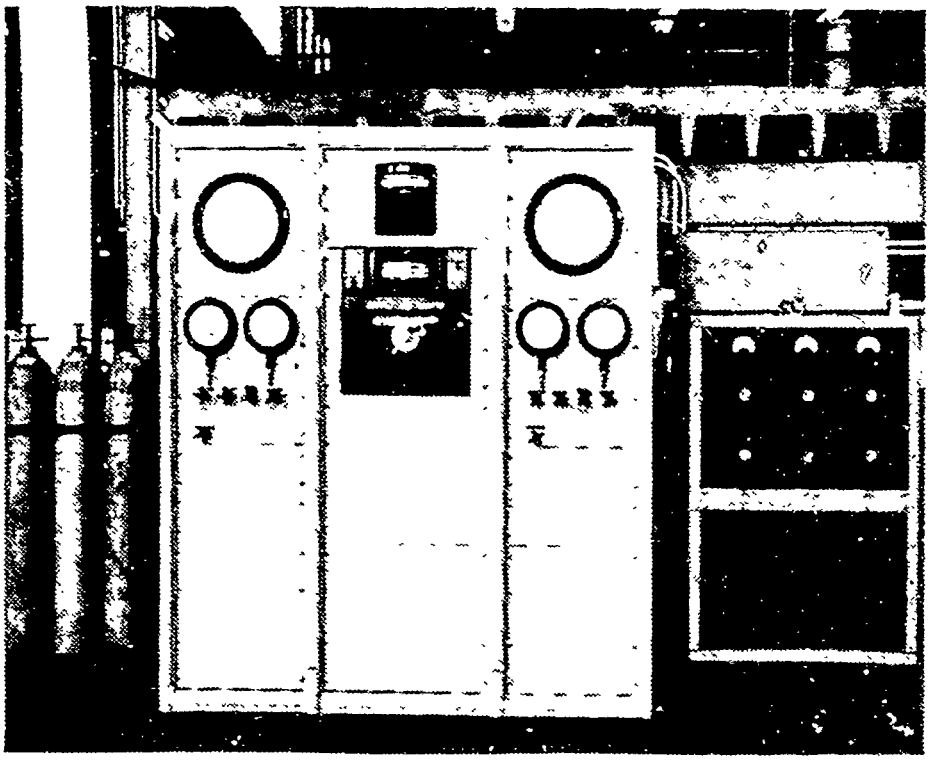


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Figure 2. Instrument Panel

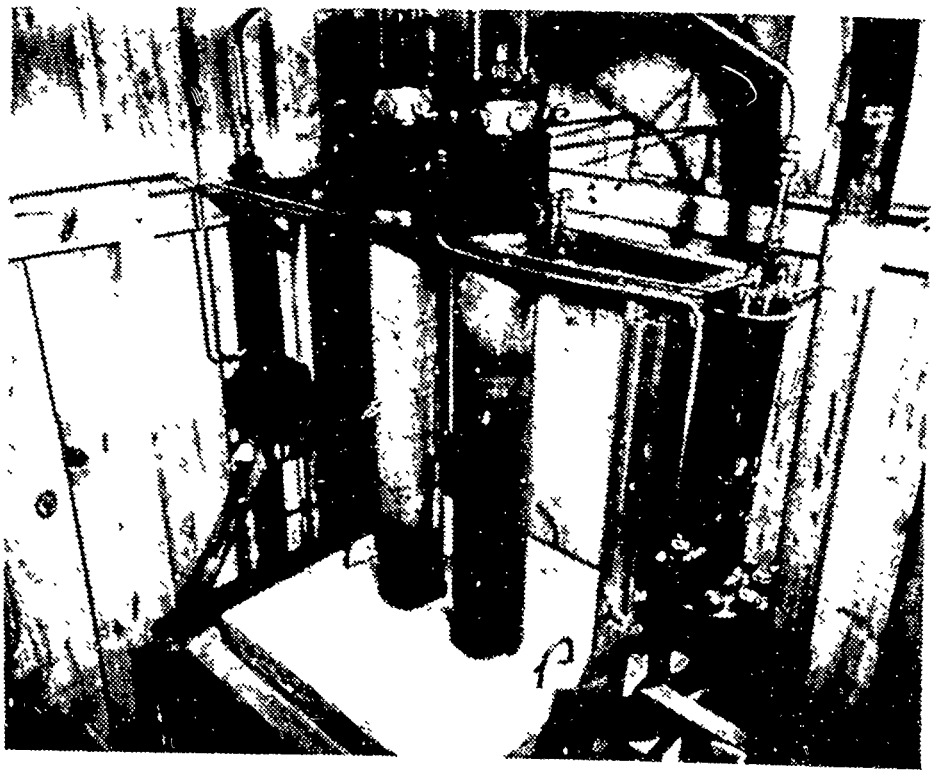

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Figure 3. Furnace, Pressure Vessels, and Condensers

(5) Stainless steel pressure tubing and fittings, to make connections with the deformable containers, pressure vessels, condensers, and pressure controlling and recording equipment.

(6) One plank and sand safety enclosure surrounding the furnace, pressure vessels, and condensers; and

(7) Appropriate instrumentation to control and record temperature and pressures.

For a typical IPB run (for example, Run No. 107-2), a mixture of graphite flour, Thermax, and pulverized pitch is mixed at 160°C, cooled, milled, reheated to 100°C, and pressed in a cylindrical mold at 7000 psi. The preformed specimen (ca. 2 5/8" diameter x 5 1/4" long) is placed with a granular packing medium in the center of a deformable container, which is then connected to the internal pressure line and lowered into one of the pressure vessels suspended in the furnace. With the crossover valve open, the external and internal pressures are increased rapidly to 1800 psig by supplying gas (vapor pumped nitrogen) from high pressure storage cylinders. The crossover valve is then closed, and the external pressure is increased to 2200 psig.

Electrical power is supplied to the furnace, the upheat rate of which is controlled by a program controller and a temperature limiting controller by means of separate thermocouples. Four temperatures, one near the top and one near the bottom of the free air space inside the furnace, and one inside of each pressure vessel adjacent to the deformable container, are recorded automatically. During the two-hour upheat to 590°C (furnace temperature) the external and internal pressures are maintained constant by manual control of the respective bleed valves. Pressures are recorded automatically.

At the end of the upheat period the internal pressure is reduced by venting on a straight line logarithmic decay schedule (one hour to one-tenth of initial pressure) to 200 psig, then rapidly (ca. five minutes) to atmospheric pressure. This results in an isostatic mechanical pressure on the deformable container, granular packing, and specimen of 2200 psi. After a four-hour holding period at maximum temperature and isostatic pressure, the power to the furnace is turned off, and the external pressure is vented rapidly (five to ten minutes) to atmospheric pressure. The standard IPB conditions (temperature and pressure vs time) described above are illustrated graphically in Figure 4.

After cooling overnight in the furnace, the deformable container is withdrawn from the pressure vessel and detached

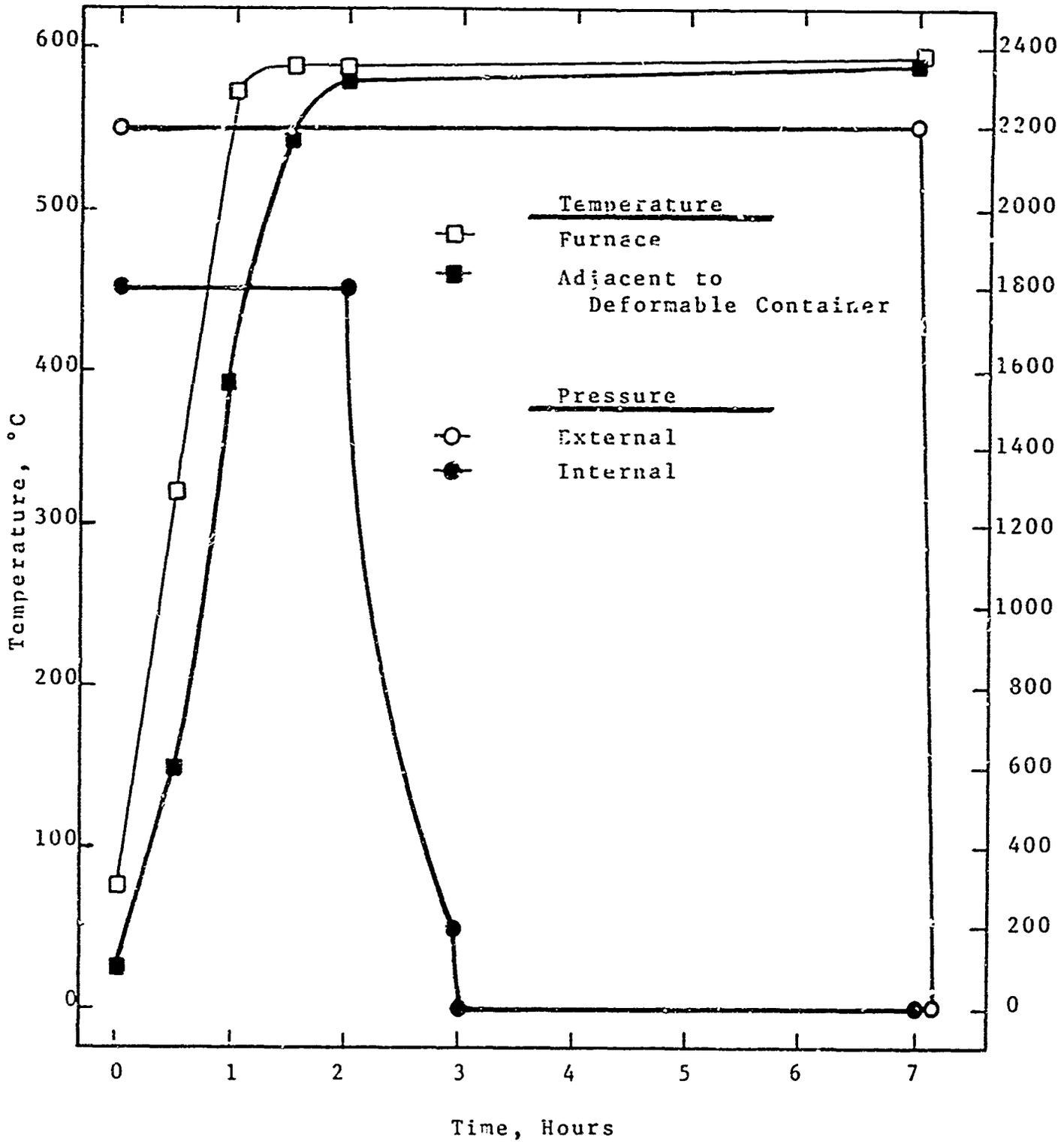

Figure 4. Standard IPB Conditions - Temperature and Pressure Vs Time

from the internal pressure line. (In Figure 5 a deformed container is shown next to a container about to be inserted in the IPB apparatus.) The specimen is removed by cutting open the container, and graphitized in a graphite tube resistance furnace at a rate of approximately 100°C per hour to 2500°C. Test procedures for evaluation of the graphitized specimens are described in Appendix II.

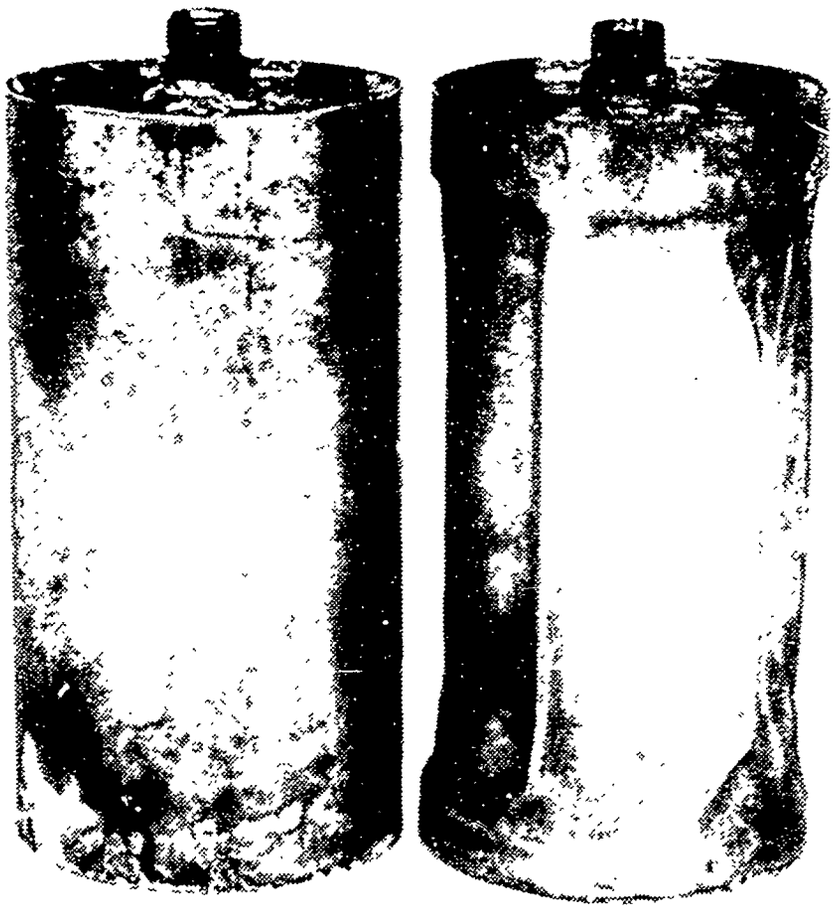

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Figure 5. Deformable Containers for IPB Specimens

3. ISOSTATIC PRESSURE BAKING EXPERIMENTS

3.1. Graphite Aggregate

Fewer processing difficulties are normally encountered with formulations including a graphite aggregate. The combination of Grade 1008 graphite flour, Thermax, and No. 30 medium coal tar pitch was chosen for the investigation of process variables in an attempt to establish optimum conditions prior to the study of other aggregates and binders. (See Appendix I for identification and properties of raw materials used in this program.)

3.1.1. Preform Density

Using two GTP (graphite flour/Thermax/pitch) formulations, preform density was varied intentionally by varying molding pressure. One might expect that, at sufficiently high isostatic mechanical pressure in the IPB run, the effect of preform density would be small. As shown in Table 1, the effect of preform density on the graphitized IPB product was minor, but was greater at the lower pitch level (23 pph) than at the higher pitch level (27 pph).

All preforms used in subsequently reported runs were molded at ca. 7000 psi which resulted in very low green porosities (less than 8% by volume). This, in turn, resulted in decreased volume reduction during the IPB run, and consequently in decreased distortion of the deformable container and specimen.

3.1.2. Upheat Rate

Holding formulation, initial pressure conditions, and venting rate constant, two upheat rates (6 hours and 2 hours to 590°C) were used. When both runs were ended after the 1-hour venting of internal gas pressure (7 hours and 3 hours total time), there appeared to be no significant difference in graphite properties. However, when a 4-hour hold at final temperature and differential pressure was added to the 2-hour upheat, 1-hour vent schedule, a significant improvement in graphite properties was obtained (see Table 2).

3.1.3. Initial Pressure Conditions

With formulation and other process conditions held constant, the initial external and internal pressures were varied widely to determine the effect on graphite properties. In the series of runs listed in Table 3 the external pressure was held at 2200 psig while the initial internal pressure was varied from 0 to 2100 psig.

TABLE 1

EFFECT OF PREFORM DENSITY (1)

Formulation	GTP 75/25/23		GTP 75/25/27	
Run No.	105-2	103-1	104-2	104-1
Preform Density, g/cc	1.60	1.78	1.65	1.77
Graphite Density, g/cc	1.85	1.88	1.88	1.89
Permeability, 10^{-2} cm^2/sec				
Axial	9.2	2.5	3.0	2.0
Radial	20	6.0	6.5	5.9
Flexural Strength, 10^3 psi				
Axial	2.98	2.83	3.31	2.36
Diametral	3.31	3.19	3.57	2.65
Compressive Strength, 10^3 psi				
Axial	8.29	8.48	9.63	9.05
Diametral	8.39	8.83	7.97	8.53

Initial external and internal pressures 2200 and 1800 psig, respectively; 6-hour upheat to 590°C furnace temperature, 1-hour venting schedule for internal pressure, no holding time at final temperature and differential pressure.

(1) Properties listed are for specimens graphitized at 2500°C.

TABLE 2

EFFECT OF UPHEAT RATE (1)

Run No.	104-1	106-2	111-2
Upheat-Vent-Hold, hrs	6-1-0	2-1-0	2-1-4
Graphite Density, g/cc	1.89	1.89	1.91
Permeability, 10^{-2} cm^2/sec			
Axial	2.0	3.6	0.67
Radial	5.9	9.8	0.71
Flexural Strength, 10^3 psi			
Axial	2.36	2.34	2.95
Diametral	2.65	3.07	3.44
Compressive Strength, 10^3 psi			
Axial	9.05	8.74	9.94
Diametral	8.53	7.26	8.81

Formulation GTP 75/25/27, preform density 1.77 to 1.79 g/cc, final furnace temperature 590°C (during vent and hold), external pressure 2200 psig throughout run, internal gas pressure 1800 psig during upheat period 1800 psig vented to atmospheric pressure in 1 hour.

(1) Properties listed are for specimens graphitized at 2500°C.

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TABLE 3

EFFECT OF INTERNAL GAS PRESSURE AT CONSTANT EXTERNAL PRESSURE (2)

Run No.	109-1	145-2	126-1	145-1	111-2	127-2
Initial Pressure, psig						
External	2200	2200	2200	2200	2200	2200
Internal	0	600	1000	1400	1800	2100
Graphite Density, g/cc	1.84	1.84	1.86	1.88	1.91	1.92
Permeability, 10^{-2} cm^2/sec						
Axial	--	2.2	1.0	0.85	0.67	1.8
Radial	--	2.9	1.3	2.4	0.71	2.6
Flexural Strength, 10^3 psi						
Axial	--	1.05	2.87	1.26	2.95	(1)
Diametral	--	1.36	3.67	1.72	3.44	4.22
Compressive Strength, 10^3 psi						
Axial	--	6.05	7.89	7.32	9.94	(1)
Diametral	--	6.44	8.64	5.93	8.81	8.63

(1) Specimen broke into three discs during the IPB run.

(2) Properties listed are for specimens graphitized at 2500°C.

Formulation GTP 75/25/27, preform density 1.78 to 1.80 g/cc, upheat rate 2 hours to 590°C, venting rate 1 hour to one-tenth of initial internal pressure (vented rapidly from 200 to 0 psig), holding time 4 to 5 hours at 590°C and 2200 psig differential (isostatic) pressure.

The beneficial effect on graphite properties of a high (up to 1800 psig) internal gas pressure is clearly illustrated. Since only one run was made at 2100 psig internal pressure, it is not known whether the disruption of this specimen (127-2) is significant. It is conceivable that the 100 psi isostatic mechanical pressure during the rapid upheat was not adequate to overcome gas pressure gradients within the specimen. At 400 psi differential pressure (1800 psig internal pressure) several other runs with this formulation have produced sound specimens.

In another series of runs with the GTP 75/25/27 formulation initial external and internal pressures were varied concurrently with a constant differential pressure of 400 psi during upheat. These runs are listed in Table 4, along with two special runs included in this table for the sake of convenience.

Comparison of several of the runs in Table 4 with several in Table 3 (compare 146-1 with 145-2, and 127-1 with 126-1) indicates that differential pressures greater than 400 psi during upheat were detrimental to product density. A possible explanation is that excessive differential (isostatic mechanical) pressure during upheat resulted in the loss of too much liquid binder from the specimen.

In runs in which the differential pressure during upheat was 400 psi, graphite product density increased regularly with external pressure up to the maximum safe operating pressure of 2200 psig. This is illustrated in Figure 6 in which the data are extrapolated to a graphite density of 1.97 g/cc at an external pressure of 10,000 psig. While the accuracy of this extrapolation may be questionable, it is not unreasonable to expect a significant decrease in porosity and permeability with increased pressure capability.

In Run No. 112-1 (Table 4) the differential pressure was 400 psi during upheat (400 psig external, 0 psig internal pressure) and was increased to 2200 psi during the normal 1-hour venting period by increasing the external pressure to 2200 psig. This resulted in a differential pressure history identical to that of the standard IPB conditions (represented by Run No. 111-2). However, the low graphite density (1.80 g/cc compared to 1.91 g/cc for 111-2) demonstrated the importance of elevated external and internal pressures during upheat.

In Run No. 128-1 (Table 4) the preformed specimen was subjected to a gas pressure bake (1800 psig during upheat) with no differential pressure during upheat or hold at 590°C. The graphite density was only 1.75 g/cc, reflecting the need for a consolidating pressure to close porosity created by departing volatile constituents. The poor structure of the graphitized specimen is illustrated in Figure 7 (compare with Run 111-2, Figure 8).

TABLE 4

EFFECT OF EXTERNAL AND INTERNAL PRESSURE AT CONSTANT DIFFERENTIAL PRESSURE (3)

Run No.	146-1	127-1	111-2	112-1	128-1
Initial Pressure, psig				(1)	(2)
External	1000	1400	2200	400	1800
Internal	600	1000	1800	0	1800
Differential Pressure, psi					
During Upheat	400	400	400	400	0
During Hold at 590°C	1000	1400	2200	2200	0
Graphite Density, g/cc	1.88	1.89	1.91	1.80	1.75
Permeability, 10^{-2} cm^2/sec					
Axial	1.3	1.4	0.67	--	170
Radial	2.7	2.4	0.71	--	290
Flexural Strength, 10^3 psi					
Axial	2.83	2.85	2.95	--	1.59
Diametral	3.48	3.74	3.44	--	1.85
Compressive Strength, 10^3 psi					
Axial	7.56	8.77	9.94	--	5.40
Diametral	8.18	8.08	8.81	--	4.96
Resistivity, 10^{-4} ohm in					
Axial	8.59	7.84	--	--	11.5
Diametral	6.30	5.39	--	--	9.02
Mod. of Elasticity, 10^5 psi					
Axial	6.84	7.39	--	--	3.73

(1) External pressure increased from 400 to 2200 psig during normal 1-hour vent period.
(2) External pressure connected to, and vented with, internal pressure.
(3) Properties listed are for specimens graphitized at 2500°C.
Formulation GTP 75/25/27, preform density 1.78 to 1.80 g/cc, upheat rate 2 hours to 590°C, 4-hour hold at 590°C.

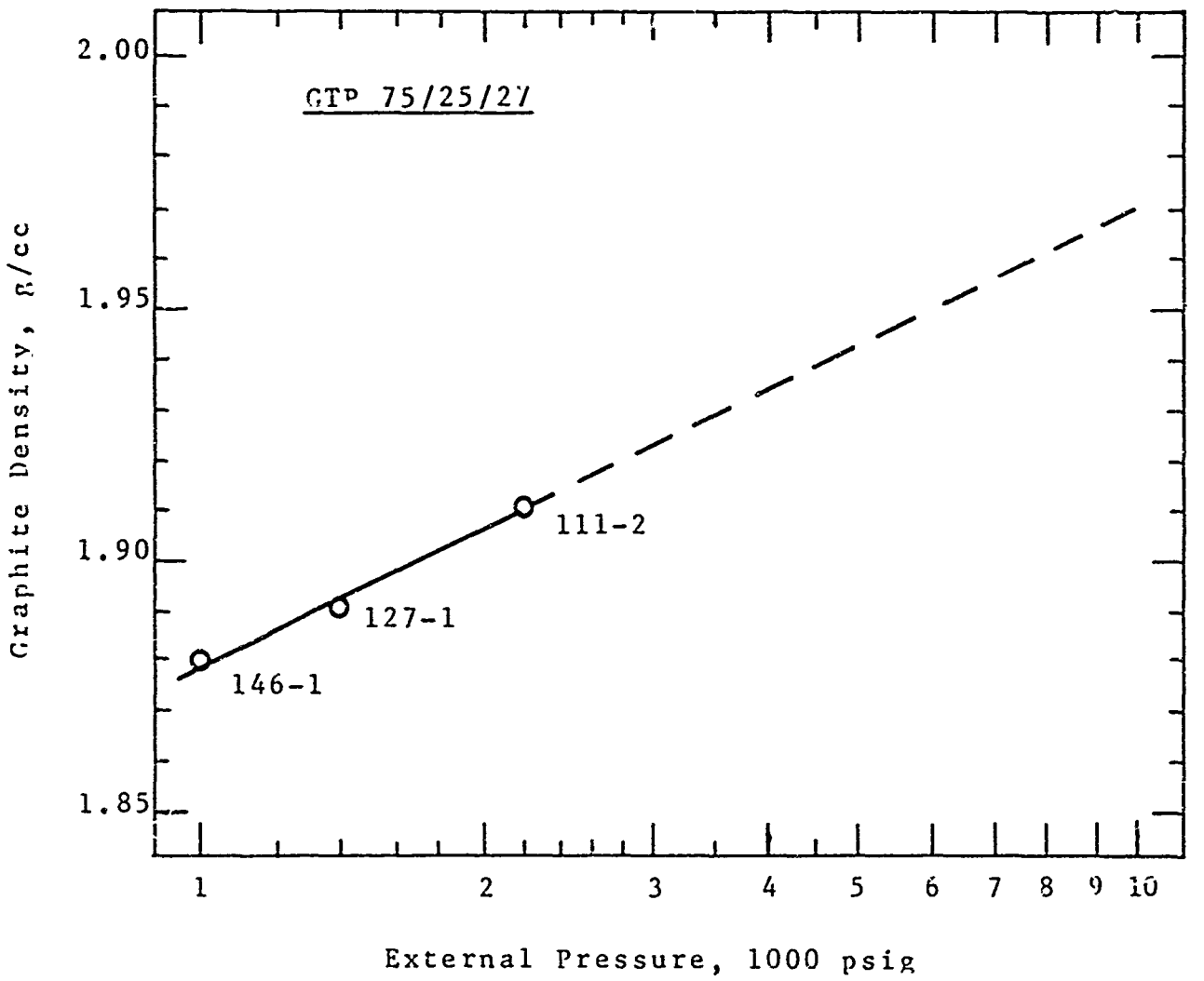
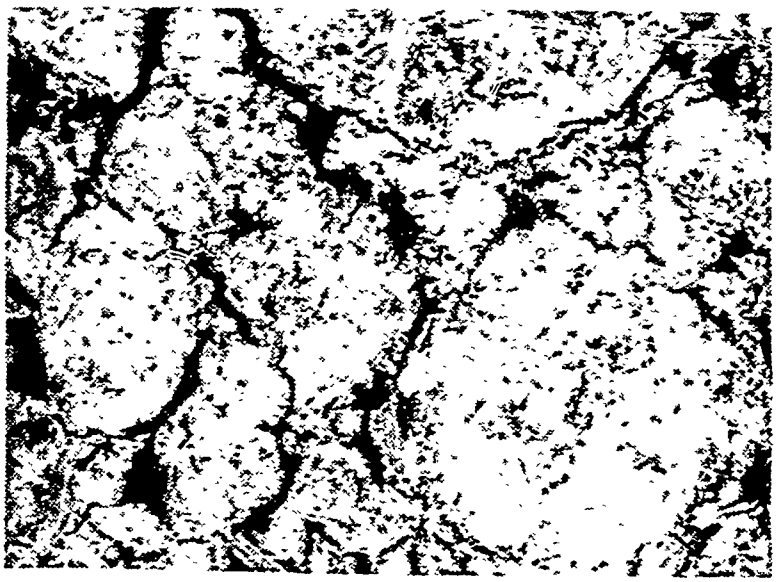


Figure 6. Graphite Density Vs. External Pressure



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Run No. 128-1 Perpendicular to Axis

100X 234-40F1

Run No. 128-1 Parallel to Axis

GTP 75/25/27, baked at 1800 psig gas pressure, no differential (isostatic mechanical) pressure during upheat or hold. Graphite Density = 1.75 g/cc.

Figure 7. Photomicrographs of GTP Specimen Baked at 1800 Psig Gas Pressure

3.1.4 Formulation

A set of standardized IPB process conditions was chosen to study the effects of variations in formulation, using aggregate G (Grade 1008 graphite flour - Great Lakes Carbon Corporation), fine filler T (Thermax - Thermatomic Carbon Company), and binder P (No. 30 medium coal tar pitch - Allied Chemical Corporation). The standard IPB conditions are summarized below:

External pressure - 2200 psig, vented rapidly to atmospheric pressure at end of run (7 hours);

Internal pressure - 1800 psig for 2 hours, vented to atmospheric pressure in 1 hour;

Furnace Temperature - heated from ambient temperature to 590°C in 2 hours, held at 590°C for 5 hours.

The above conditions are illustrated graphically in Figure 4 (Section 2).

The effect of varying Thermax level at estimated optimum binder level is shown in Table 5. The highest graphite density was obtained with 25 phc Thermax (parts Thermax per hundred parts total carbon-aggregate plus filler). Other graphite properties were relatively insensitive to Thermax level, although a few anomalies appeared. It may be assumed that the optimum pitch level at each Thermax level was not necessarily achieved by estimation. In Figure 8, the effect of varying Thermax level on the microstructure of the graphite product is illustrated. The appreciably smaller pore size in specimen 111-2 (25 phc Thermax) is readily apparent.

The effect of varying binder level from 21 to 29 phc at 25 phc Thermax is shown in Table 6. In this range, graphite properties were also relatively insensitive to binder level, with an apparent optimum level (with respect to density and permeability) at 27 phc.

3.1.5 Venting Schedule

Using the GTP 75/25/27 formulation, initial pressures of 2200 psig external and 1800 psig internal, and a 2-hour upheat to 590°C, the venting schedule was varied from 1/4 hour to 4 hours. Also, one run was made in which the initial pressures were held for 4 hours at 590°C, followed by a 1/4-hour vent. The total time of all runs was 6-1/4 to 7 hours. The process conditions and properties of the graphitized products are summarized in Table 7.

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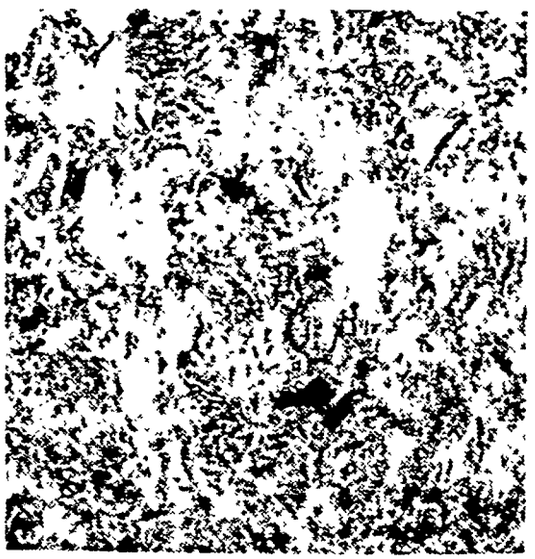
TABLE 5

EFFECT OF THERMAX LEVEL IN GTP FORMULATIONS (2)

Run No.	123-1	133-1	122-2	128-2	132-1	111-2
Formulation, Parts by Weight	GP 100/35	GTP 95/5/34	GTP 90/10/33	GTP 85/15/34	GTP 80/20/31	GTP 75/25/27
Apparent Density, g/cc						
Preform	1.79	1.79	1.81	1.81	1.80	1.79
IPB	1.89	1.86	1.72	1.90	1.88	1.86
Graphite	1.86	1.87	1.76	1.87	1.87	1.91
Permeability, 10^{-2} cm^2/sec						
Axial	1.1	1.1	51	2.1	1.3	0.67
Radial	2.4	1.8	66	6.9	4.8	0.71
Flexural Strength, 10^3 psi						
Axial	3.02	2.08	3.07	(1)	1.34	2.95
Diametral	4.07	3.00	4.02	2.31	1.64	3.44
Compressive Strength, 10^3 psi						
Axial	9.40	8.66	7.05	(1)	8.40	9.94
Diametral	7.43	7.71	7.01	6.23	6.92	8.81
Resistivity, 10^{-4} ohm in						
Axial	5.68	6.17	--	(1)	9.47	--
Diametral	3.97	4.14	--	7.34	6.80	--
Mod. of Elasticity, 10^5 psi						
Axial	--	5.24	--	(1)	3.30	--

(1) Large parabolic flaw prevented cutting of axial specimens for test.
(2) Properties listed are for specimens graphitized at 2500°C.

Standard IPB process conditions - see text.



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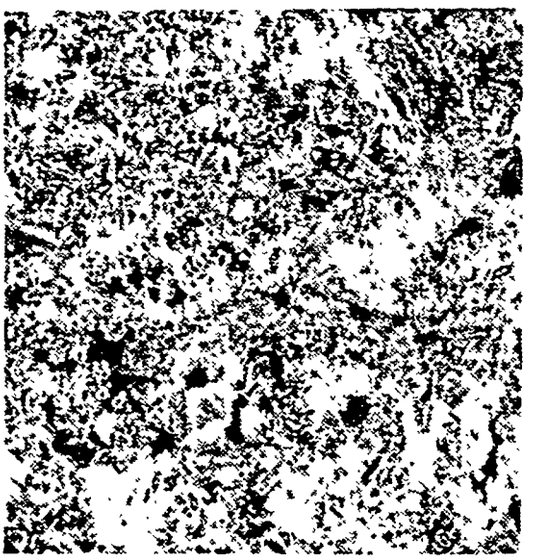

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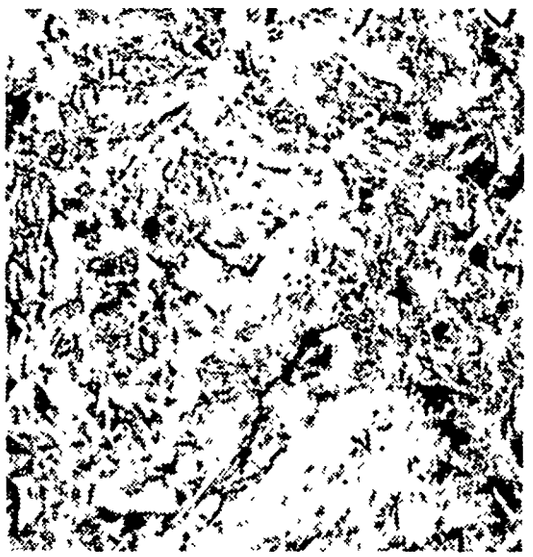
Parallel to Axis Run 123-1 Perpendicular to Axis

GP100/35, A.D. = 1.86 g/cc



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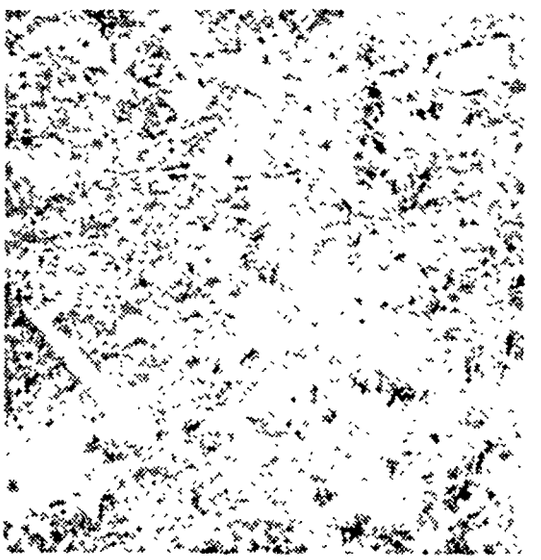

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Run 122-2	Perp. to Axis
GTP 90/10/33	A.D.=1.76 g/cc

Run 111-2	Perp. to Axis
GTP 75/25/27	A.D.=1.91 g/cc

Figure 8. Photomicrographs of IPB Graphite - Aggregate G

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TABLE 6

EFFECT OF BINDER LEVEL IN GTP FORMULATIONS (1)

Run No.	120-1	120-2	126-2	111-2	109-2
Formulation, Parts by Weight	GTP 75/25/21	GTP 75/25/23	GTP 75/25/25	GTP 75/25/27	GTP 75/25/29
Apparent Density, g/cc					
Preform	1.74	1.79	1.79	1.79	1.78
IPB	1.84	1.86	1.86	1.86	1.80
Graphite	1.89	1.90	1.90	1.91	1.85
Permeability, 10^{-2} cm^2/sec					
Axial	2.3	0.80	0.86	0.67	1.6
Radial	5.4	1.8	1.3	0.71	4.5
Flexural Strength, 10^3 psi					
Axial	2.72	2.94	2.94	2.95	2.08
Diametral	3.85	3.67	4.00	3.44	2.95
Compressive Strength, 10^3 psi					
Axial	7.28	9.11	8.84	9.94	7.61
Diametral	6.32	6.94	8.42	8.81	8.14
Resistivity, 10^{-4} ohm in					
Axial	--	--	7.92	--	--
Diametral	--	--	5.09	--	--
Mod. of Elasticity, 10^5 psi					
Axial	--	--	7.69	--	--

(1) Properties listed are for specimens graphitized at 2500°C.
Standard IPB process conditions - see text.

TABLE 7

EFFECT OF INTERNAL PRESSURE VENTING RATE (1)

Run No.	115-2	111-2	115-1	107-1
Upheat to 590°C, hours	2	2	2	2
Pre-Vent Hold, hours	0	0	0	4
Vent, hours	1/4	1	4	1
Post-Vent Hold, hours	4	4	1/4	0
Graphite Density g/cc	1.90	1.91	1.89	1.85
Permeability, 10^{-2} cm^2/sec				
Axial	0.79	0.67	0.94	1.8
Radial	2.2	0.71	1.9	4.0
Flexural Strength, 10^3 psi				
Axial	2.23	2.95	3.08	2.41
Diametral	2.84	3.44	3.91	3.20
Compressive Strength, 10^3 psi				
Axial	8.48	9.44	8.47	8.64
Diametral	7.02	8.81	8.91	8.60

Formulation GTP 75/25/27, preform density 1.78 to 1.80 g/cc, initial pressures 2200 psig external and 1800 psig internal.

(1) Properties listed are for specimens graphitized at 2500°C.

Graphite properties were relatively insenstivie to the venting schedule, although the 1-hour vent appears to be slightly better than either extreme. With a very rapid vent (less than 1/4-hour), disruptive pressure gradients within the specimen might develop. With a very slow vent (appreciable more than 4 hours), polymerization might occur to the extent that maximum differential pressure would be applied too late to compress the specimen to maximum density. This phenomenon is demonstrated in Run 107-1 in which the initial pressure conditions (2200 psig external, 1800 psig internal, 400 psi differential) were held for 4 hours at 590°C before venting. The product density was 1.85 g/cc (compared to 1.91 g/cc for Run No. 111-2).

3.1.6 Holding Time at Maximum Differential Pressure

In Table 8 a group of five runs is presented in which the only variable was the holding time at 590°C after venting the internal gas pressure to 0 psig.

Although the effect of holding time appears to be somewhat erratic, the 4-hour hold chosen as standard resulted in the optimum graphite properties. It is quite apparent that at the end of the 2-hour upheat and 1-hour vent, the specimen had not become sufficiently rigid to resist further consolidation (at 2200 psig differential pressure).

3.1.7 Final Furnace Temperature

The maximum safe operating pressure of the pressure vessels used in this program is dependent on the operating temperature. Various considerations led to the choice of 590°C as the operating temperature, at which temperature the pressure rating is 2200 psig. Extrapolation of the data presented in Table 4 (Runs 146-1, 127-1, and 111-2) indicated that an improvement in graphite density may be expected by an increase in the pressure capability of the IPB process at 590°C. In order to determine whether increasing the temperature capability would be helpful, a pair of runs was made at 620°C and 1800 psig. These runs, along with several runs at lower temperatures (560°, 575°, and 595°C) are listed in Table 9 and illustrated graphically in Figure 9.

Figure 9 shows that 590°C is a critical temperature for the IPB process, at least for the formulation and other process conditions used here. While a significant improvement in graphite density and other properties resulted from an increase in process temperature from 560°C to 590°C, no further improvement resulted from an increase to 620°C at slightly reduced process pressure.

The two runs made at 620°C were made simultaneously in separate pressure vessels. To avoid the possibility of having

TABLE 8

EFFECT OF HOLDING TIME AT MAXIMUM DIFFERENTIAL PRESSURE (1)

Run No.	106-2	125-1	134-1	124-1	143-1
Upheat to 590°C, hours	2	2	2	2	2
Vent, hours	1	1	1	1	1
Hold at 590°C, hours	0	1	2	4	8
Graphite Density, g/cc	1.88	1.85	1.84	1.91	1.88
Permeability, 10^{-2} cm^2/sec					
Axial	3.6	2.8	9.4	0.47	2.1
Radial	9.8	6.1	8.2	1.0	2.3
Flexural Strength, psi					
Axial	2.34	2.48	1.66	3.08	2.79
Diametral	3.07	2.26	1.42	3.80	3.08
Compressive Strength, psi					
Axial	8.74	7.32	7.54	8.50	8.01
Diametral	7.26	7.67	6.37	9.03	8.02
Resistivity, 10^{-4} ohm in					
Axial	--	8.81	10.2	7.40	8.62
Diametral	--	7.06	7.84	5.85	6.48
Mod. of Elasticity, 10^5 psi					
Axial	--	6.07	4.95	--	7.27

Formulation GTP 75/25/27, preform density 1.77 to 1.81 g/cc, initial pressure 2200 psig external and 1800 psig internal.

(1) Properties listed are for specimens graphitized at 2500°C.

TABLE 9

EFFECT OF FINAL FURNACE TEMPERATURE (1)

Run No.	130-1	140-2	124-1	151-1	151-2
Final Furnace Temp., °C	560	575	590	620	620
Container Temp., °C					
At Start of Vent	555	570	585	615	570
During Hold	560	575	590	620	620
Time Schedule, hours					
Upheat	2	2	2	2	1-1/2
Vent	1	1	1	1	1
Hold	4	4	4	4	4-1/2
Graphite Density, g/cc	1.82	1.87	1.91	1.91	1.89
Permeability, 10^{-2} cm^2/sec					
Axial	12	0.73	0.47	0.95	0.80
Radial	9.7	1.45	1.0	1.3	1.5
Flexural Strength, 10^3 psi					
Axial	1.95	1.78	3.08	2.89	2.93
Diametral	1.89	1.64	3.80	3.53	3.52
Compressive Strength, 10^3 psi					
Axial	7.94	7.62	8.50	7.51	7.31
Diametral	6.66	6.73	9.03	7.57	8.51
Resistivity, 10^{-4} ohm in					
Axial	9.96	9.84	7.40	8.46	8.41
Diametral	9.18	7.67	5.85	6.56	6.54
Mod. of Elasticity, 10^5 psi					
Axial	4.23	5.31	--	6.95	--

(1) Properties listed are for specimens graphitized at 2500°C.

Formulation GTP 75/25/27, preform density 1.79 to 1.80 g/cc.

Initial pressure 2200 psig external, 1800 psig internal for Runs 130-1, 140-2, and 124-1; 1800 psig external, 1500 psig internal for Runs 151-1 and 151-2.

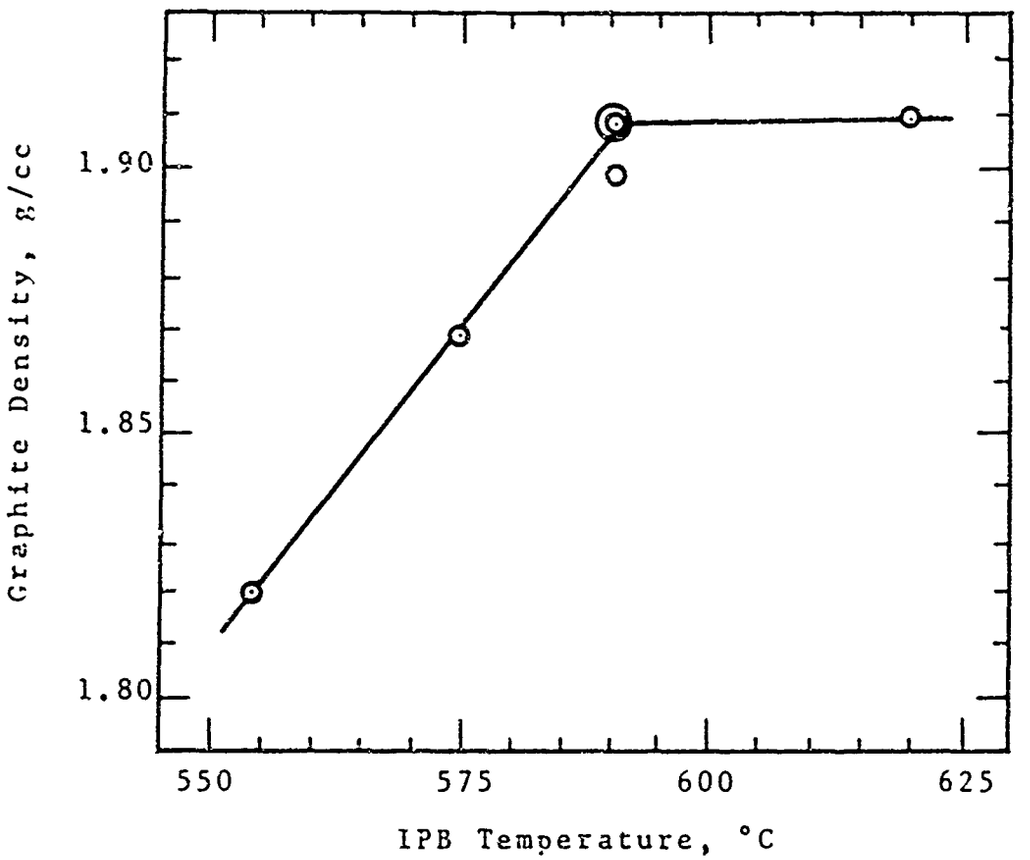

Figure 9. Graphite Density Vs. IPB Temperature

both specimens set to a rigid structure at the higher temperature before maximum differential pressure could be applied, the internal venting on one run was begun before final temperature was reached (see Table 9 - Container Temperature at Start of Vent). Although the graphite densities of the two specimens were not identical (1.91 and 1.89 g/cc), the agreement between the two in all other properties tested was very good.

3.1.8 Isostatically Molded Preforms

Two GTP specimens were molded within impermeable membranes at 100°C by application of isostatic (hydraulic) pressure. Both were subjected to the standard IPB process conditions (Figure 4). In Table 10 the graphite properties are listed with those of three standard preforms (pressed axially in a cylindrical mold). The isostatic preforms finished to an approximate diameter of 3-5/8 inches. One (139-1) was used as molded, while the other (135-1) was first machined to 2-5/8 inch diameter (same size as standard preforms).

Two wholly unexpected results were obtained with the isostatic preforms; first, the graphite density and other properties were inferior to those of the standard preforms, and secondly, the isotropy of properties was not improved. No plausible explanation is offered.

3.1.9 Uniformity and Reproducibility

The size of the IPB specimens and the scope of the program did not permit a thorough study of uniformity and reproducibility of properties. An overall pooled standard deviation for each of the properties measured, for all specimens in the program, would not be meaningful since the majority of the specimens were processed at conditions which were not optimum.

Three specimens (107-2, 111-2, and 124-L, Table 10) were made with the GTP 75/25/27 formulation under standard IPB conditions. The uniformity of graphite density of specimen 107-2 was determined. The overall density was 1.90 g/cc. The density of the 2 in. diam. x 1-1/2 in. long permeability specimen machined from one end was 1.914 g/cc. The densities of three 1/2 in. x 1/2 in. x 2-3/8 in. prisms (diametral test specimens) cut from near the center (with respect to the axis of the whole specimen) were 1.877, 1.873, and 1.874 g/cc. The densities of three 1/2 in. x 1/2 in. x 3-5/8 in. prisms (axial test specimens covering approximately two-thirds of the axial length of the whole specimen) were 1.882, 1.889, and 1.890 g/cc. From this it may be assumed that the specimen had an axial density range of ca. 1.91 g/cc near the ends to 1.87 near the center. The radial density gradient was not established.

TABLE 10

GRAPHITE PROPERTIES[1] STANDARD AND ISOSTATIC PREFORMS

	Standard Preforms			Isostatic Preforms	
Run No.	107-2	111-2	124-1	135-1	139-1
Preform Density, g/cc	1.78	1.79	1.79	1.79	1.80
Graphite Density, g/cc	1.90	1.91	1.91	1.86	1.89
Permeability, 10^{-2} cm^2/sec					
Axial	1.8	0.67	0.47	3.3	5.0
Radial	4.0	0.71	1.0	7.9	8.6
Flexural Strength, 10^3 psi					
Axial	2.91	2.95	3.08	1.53	2.68
Diametral	3.38	3.44	3.80	1.77	2.99
Compressive Strength, 10^3 psi					
Axial	7.70	9.94	8.50	7.30	9.13
Diametral	8.30	8.81	9.03	6.25	8.46
Resistivity, 10^{-5} ohm in					
Axial	--	--	7.40	9.21	7.18
Diametral	--	--	5.85	7.57	6.54
Mod. of Elasticity, 10^5 psi					
Axial	--	--	--	4.99	8.16
Diametral	--	--	--	--	9.38

(1) Graphitized at 2500°C.

Formulation GTP 75/25/27.

Standard IPB process conditions.

A statistical analysis of the variation of flexural strengths of specimens 107-2, 111-2, and 124-1 is presented in Table 11. Standard deviations were calculated on a rigorous basis, sacrificing one degree of freedom for each calculated mean value. The pooled standard deviations of individual values from the group means (three individual values in each of three groups) were 104 psi (3.5%) for axial flexural strength, and 197 psi (5.6%) for diametral flexural strength. The standard deviations of individual values from the overall mean (nine values, eight degrees of freedom) were 117 psi (3.9%) for axial values and 261 psi (7.4%) for diametral values. Standard deviations of group means from the overall mean were 119 psi (4.0%) and 228 psi (6.4%), respectively.

It is apparent from inspection of Table 10 that the piece to piece reproducibility of permeability and compressive strength was not as good as that of flexural strength. This may be the fault of either specimen preparation or testing procedure. For example, the compressive strength specimens were prepared from the broken ends of the flexural strength specimens. If any of the specimens contained cracks generated in the flexural test, lower compressive strengths would have resulted.

As pointed out in 3.1.7., the reproducibility between mean values of all properties, except density, for the two specimens (Runs 151-1 and 151-2, Table 9) processed at 620°C was remarkably good. This fact points to the probability that the excellent reproducibility obtained at standard IPB conditions would be further improved by an increase in the process temperature to 620°C.

3.1.10. High Softening Point Pitches

Two coal tar pitches having higher carbon yields than the standard pitch binder (see Appendix 1) were available for this program; an experimental grade, designated "O" pitch and a commercial grade, designated "Q" pitch. Unfortunately, both pitches suffered the processing disadvantage of having very high softening points. GTO and GTQ 75/25/27 mixes were made at 220°C. On molding at 170° to 190°C, very low preform densities resulted. The mixes were repeated, with the addition of trichloroethylene to soften the mix at room temperature, followed by application of heat in the mixer to evaporate the solvent. Upon milling the mixture and molding at approximately 180°C, excellent preforms (preform density = 1.79 g/cc) were obtained. However, both specimens cracked into three pieces in the IPB process. The apparent densities of the broken pieces, measured by water immersion, averaged 1.91 g/cc for both specimens. Physical properties were not determined.

It was surmised that the difficulty may have been the result of altered rheology of the pitches due to chlorination by the solvent used to decrease viscosity during mixing. Consequently, the

TABLE 11

STATISTICAL ANALYSIS OF FLEXURAL STRENGTHS - STANDARD FORMULATION AND IPB PROCESS CONDITIONS(1)

		Flexural Strength, psi	
		Axial	Diam.
Run 107-2		2990	3420
		2930	3380
		2810	3350
Group Mean		2910	3383
Standard Deviation,	psi	92	35
	per cent	3.2	1.0
Run 111-2		2820	3530
		2970	3460
		3060	3330
Group Mean		2950	3440
Standard Deviation,	psi	129	101
	per cent	4.4	2.9
Run 124-1		3130	3430
		2980	4000
		3130	3980
Group Mean		3080	3803
Standard Deviation,	psi	87	323
	per cent	2.8	8.5
Pooled St. Dev. of Individual Values From Group Means,	psi	104	197
	per cent	3.5	5.6
Overall Mean, psi		2980	3542
St. Dev. of Group Means from Overall Mean,	psi	119	228
	per cent	4.0	6.4
St. Dev. of Individual Values from Overall Mean,	psi	117	261
	per cent	3.9	7.4

(1) Properties listed are for specimens graphitized at 2500°C.

mixes were again repeated, using benzene instead of trichloroethylene. The preforms appeared sound but densities were somewhat lower (1.70 g/cc for GT and 1.77 for GTQ). In standard IPB runs the GTO specimen cracked into many pieces, while the GTQ was apparently sound. However, on graphitization the GTO specimen also broke into several pieces, and it was not possible to determine all physical properties. The density (1.91 g/cc), diametral flexural strength (3920 psi), diametral compressive strength (8170 psi) and axial and radial permeabilities (1.0 and 4.5 x 10^{-2} cm^2/sec, respectively), were approximately equivalent to those of the GTP 75/25/25 specimens using standard IPB conditions (Runs 107-2, 111-2, and 124-1).

While no improvement for the use of high softening point pitches is indicated by the above experiments, it is quite probable that the optimum IPB process conditions are different than for the standard pitch. Time available did not permit the establishment of these conditions.

3.2 Calcined Petroleum Coke Aggregate

The standard IPB conditions (Figure 4) were used to evaluate a series of formulations incorporating aggregate C (calcined petroleum coke flour - see Appendix I), fine filler T (Thermax), and binder P (No. 30 medium coal tar pitch). The Thermax level was varied from 0 to 25 phc, and pitch level was adjusted by judgment of mix appearance. The results are tabulated in Table 12.

The CP 100/32 formulation (Run 122-1) produced graphite properties essentially equivalent to those of the corresponding member of the G flour series (GP 100/35, Run 123-1, Table 5). At 25 phc Thermax (Runs 146-2, 110-2, and 110-1), graphite properties were somewhat inferior to the properties of all GTP formulations containing 25 phc Thermax (five binder levels - Table 6). At all intermediate Thermax levels (5, 10, 15, and 20 phc), the graphitized IPB specimens were less dense, and were extremely weak. With most of these specimens, a type of expansion failure during graphitization occurred which is seldom found in samples of such small size. In an attempt to alleviate this condition, two of the formulations (CTP 95/5/34 and 85/15/31) were repeated (Runs 141-2 and 141-1), but the IPB specimens were graphitized at one-half the standard rate. This resulted in no improvement.

Photomicrographs of three of the graphite specimens are shown in Figure 10. The CP 100/32 specimen (Run 122-1) is sound, with relatively few elongated pores. There is little difference between the appearances of the sections parallel and perpendicular to the axis (of the original cylindrical specimen).

TABLE 12

CALCINED PETROLEUM COKE FORMULATIONS - STANDARD IPB CONDITIONS[3]

Run No.	122-1	131-2	141-2[1]	129-1	131-1	141-1[1]	132-2	146-2	110-2	110-1
Formulation, Parts by Weight	CP 100/32	CTP 95/5/34	CTP 95/5/34	CTP 90/10/30	CTP 85/15/31	CTP 85/15/31	CTP 80/20/24	CTP 75/25/26	CTP 75/25/24	CTP 75/25/
Apparent Density, g/cc										
Preform	1.68	1.67	1.68	1.72	1.74	1.71	1.74	1.74	1.75	1.73
IPB	1.88	1.77	1.77[2]	1.76[2]	1.78	1.77[2]	1.72	1.74[2]	1.79	1.76
Graphite	1.88	1.80	1.75	1.69	1.74	1.79	1.77	1.77	1.88	1.86
Permeability, 10^{-2} cm^2/sec										
Axial	1.5	--	170	310	--	32	--	--	3.7	8.7
Radial	2.0	--	250	330	--	59	--	--	10	24
Flex. Strength, 10^3 psi										
Axial	3.07	--	0.49	--	--	0.14	--	--	1.83	2.12
Diametral	4.11	--	1.09	--	--	0.18	--	--	2.41	2.56
Comp. Strength, 10^3 psi										
Axial	7.04	--	5.01	--	--	2.45	--	--	7.81	7.70
Diametral	6.23	--	3.72	--	--	2.06	--	--	7.33	6.85
Resistivity, 10^{-4} ohm in										
Axial	--	14.7	14.7	--	--	40.9	--	--	--	--
Diametral	--	8.78	9.41	--	--	27.0	--	--	--	--

(1) Specimen graphitized to 2500°C at slower rate, 50°C/hr instead of 100°C/hr.

(2) Specimen broke in two during IPB

(3) All except 141-2 and 141-1 graphitized at 2500°C at a rate of 100°C per hour.

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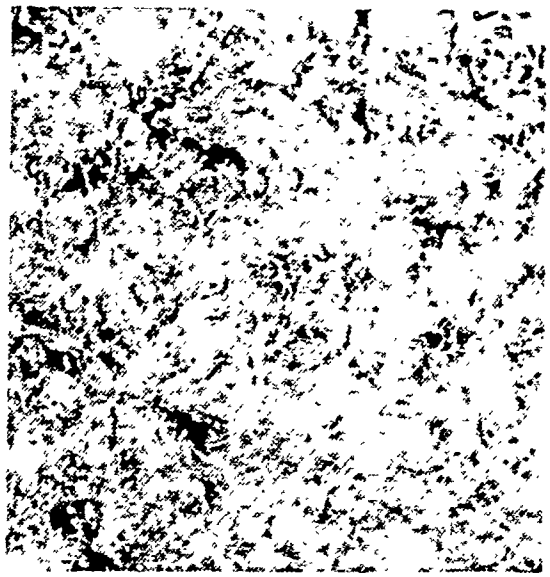

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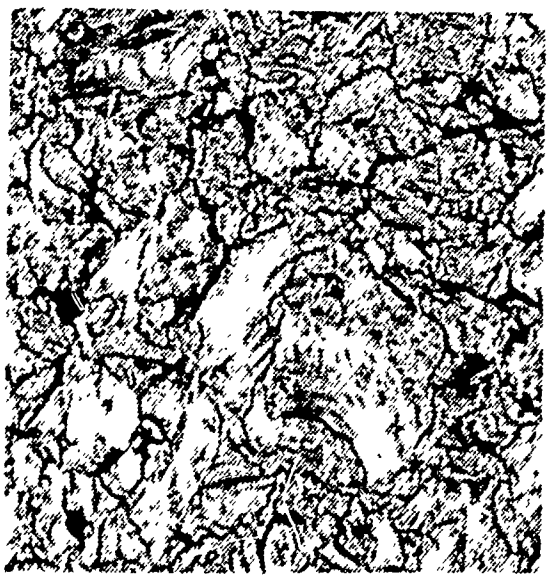
Parallel to Axis Run 122-1 Perpendicular to Axis

CP100/32, A.D. = 1.88 g/cc



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Run 129-1 Perp. to Axis

CTP 90/10/30 A.D.=1.69 g/cc

100X 234-39A3

Run 110-2 Perp. to Axis

CTP 75/25/24 A.D.=1.88 g/cc

Figure 10. Photomicrographs of IPB Graphite - Aggregate C

The reason for the low strengths of the CTP specimens at the intermediate Thermax levels is apparent in the photomicrograph of the CTP 90/10/30 (Run 129-1) specimen. Complete disruption into fragments is suggested, although the specimen was sufficiently strong to permit machining of the permeability specimen. The CTP 75/25/24 (Run 110-2) specimen appears to have undergone partial disruption, although flexural strengths were fairly respectable (1830 psi axial, and 2410 psi diametral).

Flexural strength aniostropy ratios (diametral/axial) of the three best specimens (122-1, 110-2, and 110-1) averaged 1.29 (1.21 to 1.34 range).

Hindsight now makes it apparent that much of the time spent on the runs at intermediate Thermax levels might have been expended more profitably on formulations with no Thermax, or with 25 phc or more Thermax.

3.3 Isotropic Aggregates

Three carbon flour aggregates of relatively isotropic nature were included in the IPB program. The probability of greater shrinkage in graphitization and decreased isotropy of properties for one or more of the aggregates was anticipated. Aggregate V was prepared by milling calcined Gilsonite coke obtained from the American Gilsonite Company. Aggregates R and S were primarily of petroleum origin, and were previously developed under company sponsored research. Identification and properties of all raw materials used in this program are listed in Appendix I. Photomicrographs of 65/100 mesh fractions (suspended in an optical grade resin) of each of the five flours are presented in Appendix I as Figures 14, 15, 16, 17, and 18.

On the basis of microstructure, the aggregates can be classified into three distinct groups. Aggregates G (graphite flour) and aggregate C (calcined petroleum coke flour) are very similar, and show the relatively large, orderly domains of graphite structure typical of most petroleum cokes produced by the delayed coking process. This similarity is to be expected, since the major portion of the synthetic graphite stock from which aggregate G was produced consisted of calcined petroleum coke aggregate.

The large orderly domains in aggregates G and C are primarily responsible for the anisotropy of properties in graphite articles produced from these aggregates by conventional techniques. Typically, the CTE (coefficient of thermal expansion) of extruded graphite is low (Appendix I).

The microstructure of aggregate V (calcined Gilsonite coke)

is in a class by itself, showing complete disorder or randomness as far as graphitic structure is concerned. The CTE of extruded graphite containing aggregate V (Appendix I) is high, and the appearance of the aggregate suggests that any graphite produced from it should be essentially isotropic. That this is not quite true will be pointed out later.

The microstructures of aggregates R and S, developed under company sponsored research, are quite similar, and these aggregates constitute the third classification. The dense, rounded grains have a uniform microstructure with very small domains of graphitic structure. Moreover, these small domains appear to have completely random orientation with respect to each other within any particle. Therefore graphites produced from these aggregates may be expected to be isotropic, as is indeed the case. The CTE's of extruded graphites made from aggregates R and S are relatively high, but not as high as those made from aggregate V (Appendix I).

A series of ten mixes incorporating aggregate V (calcined Gilsonite flour), with 0 to 25 phc Thermax, and binder P was processed using the standard IPB conditions. The results are given in Table 13. As was the case with the CTP series (Table 12), the best graphite properties were obtained using formulations containing 0 and 25 phc Thermax, while formulations containing 5, 10, and 15 phc produced very weak graphite specimens. The VP 100/32 formulation (Run 118-1) resulted in graphite having flexural strengths of 4020 and 5380 psi (axial and diametral, respectively). These flexural strengths were higher than any obtained in the GTP or CTP series, but lower than several of the RTP and STP series (Table 14). The compressive strengths of the VP 100/32 graphite specimen were 16,400 and 16,100 psi, which were higher than all other compressive strengths obtained in the program.

Photomicrographs of the VP 100/32 (Run 118-1) and VTP 90/10/33 (Run 119-2) specimens are presented in Figure 11. The completely random microstructure of this aggregate is again visible in these figures. The former appears to consist of large dense areas partially surrounded by elongated, curved voids. The latter consists of dense areas completely surrounded by relatively straight fissures meeting at sharp angles.

Although the microstructure of the specimens containing aggregate V suggests isotropy of properties, the flexural strength isotropy ratio (diametral/axial) of the three best specimens (118-1, 116-2, and 116-1) averaged 1.29 (1.25 to 1.34 range), which is essentially identical to that of the aggregate C (calcined petroleum coke) series.

In Table 14 the results are given for standard IPB processing of four mixes containing aggregate S and six mixes

TABLE 13

CALCINED GILSONITE COKE FORMULATIONS - STANDARD IPB CONDITIONS [3]

Run No.	147-1	~~118-1~~	149-2	149-1	119-2	142-2	144-2	144-1	116-2	116-1
Formulation, Parts by Weight	VP 100/35	VP 100/32	VTP 95/5/34	VTP 95/5/31	VTP 90/10/33	VTP 90/10/30	VTP 85/15/31	VTP 85/15/28	VTP 75/25/28	VTP 75/25/25
Apparent Density, g/cc										
Preform	1.68	1.65	1.64	1.66	1.69	1.65	1.69	1.63	1.70	1.67
IPB	1.66[1]	1.74	1.73	1.72	1.75	1.73[1]	1.68	1.72	1.70	1.70
Graphite	1.74	1.92	1.80	1.86	1.90[2]	1.85	1.81	1.85	1.91	1.91
Permeability, 10^{-2} cm^2/sec										
Axial	--	2.2	140	33	18	95	29	99	0.96	1.3
Radial	140	3.9	120	74	38	140	32	120	2.3	3.3
Flex. Strength, 10^3 psi										
Axial	0.15	4.02	0.52	0.30	--	0.60	0.14	0.37	3.43	3.53
Diametral	0.17	5.38	0.73	0.59	0.82	0.73	0.30	0.29	4.30	4.61
Comp. Strength, 10^3 psi										
Axial	3.41	16.4	6.88	3.98	--	8.66	3.11	4.46	10.6	11.8
Diametral	3.11	16.1	4.90	4.07	5.62	6.98	3.92	4.80	12.1	13.6
Resistivity, 10^{-4} ohm in										
Axial	21.6	--	17.3	21.6	--	14.9	26.1	--	--	--
Diametral	20.1	--	11.7	14.3	--	11.4	19.4	19.4	--	---

(1) Specimen broke in two during IPB.

(2) Graphite specimen broke during machining.

(3) Properties listed are for specimens graphitized at 2500°C.

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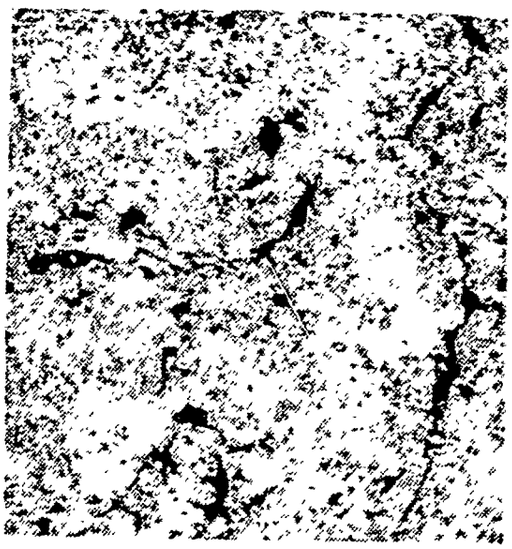
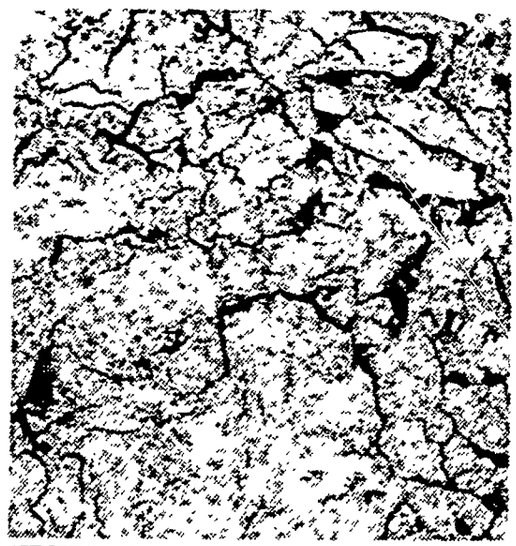


100X 234-40A3

Run 118-1 Perp. to Axis
VP 100/32 A.D.=1.92 g/cc



100X 234-40D3

Run 110-2 Perp. to Axis
VTP 90/10/33 A.D.=1.90 g/cc

Figure 11. Photomicrographs of IPS Graphite - Aggregate V

TABLE 14

FORMULATIONS WITH ISOTROPIC AGGREGATES R AND S - STANDARD IPB CONDITIONS[2]

Run No.	117-2	119-1	112-2	113-1	117-1	118-2	129-2	137-1	113-2	114-1
Formulation, Parts by Weight	SP 100/32	STP 90/10/33	STP 75/25/28	STP 75/25/25	RP 100/35	RTP 90/10/32	RTP 85/15/31	RTP 80/20/29	RTP 75/25/30	RTP 75/25/27
Apparent Density, g/cc										
Preform	1.73	1.77	1.74	1.74	1.63	1.64	1.65	1.64	1.68	1.60
IPB	1.82	1.81	1.79	1.80	1.69	1.72	1.73	1.73[1]	1.71	1.68
Graphite	1.90	1.90	1.94	1.96	1.89	1.95	1.96	1.96	1.96	1.94
Permeability, 10^{-2} cm^2/sec										
Axial	3.4	2.2	3.9	2.0	5.0	1.1	6.3	0.77	2.0	2.9
Radial	7.6	4.7	3.5	4.7	13	2.3	3.4	1.9	3.6	7.0
Flex. Strength, 10^3 psi										
Axial	4.52	5.41	3.71	2.80	1.83	6.48	4.99	4.28	3.83	4.08
Diametral	5.07	5.46	3.62	2.99	2.22	7.20	5.55	4.40	4.15	4.08
Comp. Strength, 10^3 psi										
Axial	11.1	10.8	11.7	12.6	10.7	14.3	13.6	13.8	13.8	12.3
Diametral	11.7	9.76	12.0	11.6	9.25	15.9	12.8	11.5	13.6	11.6
Resistivity, 10^{-4} ohm in										
Axial	--	--	--	--	--	--	4.51	6.83	--	--
Diametral	--	--	--	--	--	--	4.33	5.79	--	--
Mod. of Elasticity, 10^5 psi										
Axial	--	--	--	--	--	--	9.94	--	--	---

(1) Specimen broke in two during IPB.

(2) Properties listed are for specimens graphitized at 2500°C.

containing aggregate R. Graphite flexural strengths and densities were higher than for any of the other aggregates used in the program. The RTP 90/10/32 specimen (Run 118-2) had flexural strengths of 6480 and 7200 psi (axial and diametral, respectively). Seven of the ten specimens had densities in the 1.94 to 1.96 g/cc range. Compressive strengths were consistently high (14,300 and 15,900 psi for specimen 118-2), though none were as high as those of the VP 100/32 specimen (118-1, Table 13). Permeabilities were consistently low (10^{-2} to 10^{-1} cm^2/sec), but not quite as low as some of the GTP specimens. The flexural strength anisotropy ratios (diametral/axial) averaged 1.06 (0.98 to 1.22 range), and were the lowest of all aggregates tested.

Photomicrographs of several of the graphite specimens made using aggregates S and R appear in Figures 12 and 13. The reason for the somewhat lower flexural strengths (1830 psi axial, 2220 psi diametral) of specimen 117-1 is apparent in Figure 13. The fissures which are revealed are quite extensive, but discontinuous. The specimens exhibit a fine uniform pore structure. The small domains of orderly graphitic structure within the aggregate particles are readily apparent. In view of the high degree of isotropy, it must be assumed that the orientation of the orderly domains is essentially random on the macro scale, in spite of the high uniaxial pressure (7000 psi) used in molding the preforms.

3.4 Coefficient of Thermal Expansion

One method which is used to evaluate the degree of orientation of a carbonaceous aggregate is to extrude a pitch bonded mixture into small cylindrical rods, bake, graphitize, and measure the CTE (coefficient of thermal expansion). A low CTE measured in the axial direction indicates a high degree of orientation, while a high CTE indicates a relatively isotropic aggregate. The values measured in this way are listed in Appendix I - Characterization of Raw Materials, for each of the five flour aggregates used in the program. Representative IPB graphite specimens were also selected for determination of CTE, in both the axial and diametral directions. The results are tabulated in Table 15, with the extruded rod CTE values included for comparison.

The following observations are made, concerning the data in Table 15; (1) the same relative CTE order exists for the five aggregates with both the extruded rod and IPB specimen values, (2) the axial IPB values are higher than the diametral in all cases, with aggregates G and C exhibiting relatively high anisotropy ratios, and aggregates V, R, and S exhibiting relatively low anisotropy ratios, and (3) the addition of Thermax

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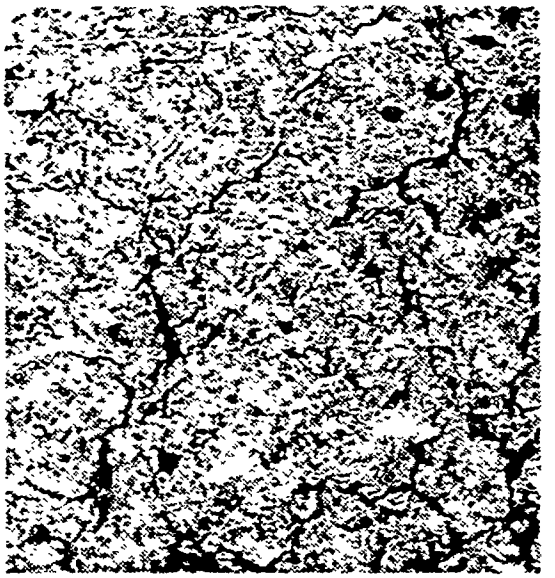
100X 234-41C1

Run 117-2 Perp. to Axis
STP 100/32 A.D.=1.90 g/cc

100X 234-40C3

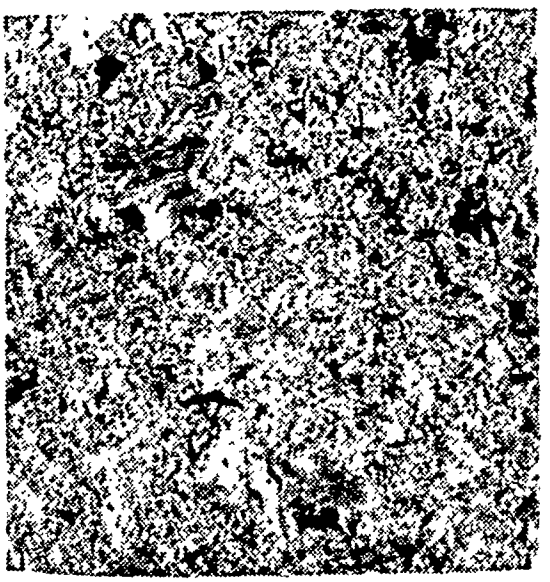
Run 119-1 Perp. to Axis
STP 90/10/33 A.D.=1.90 g/cc

Figure 12. Photomicrographs of IPB Graphite - Aggregate S



100X 234-41B1

Run 117-1 Perp. to Axis
RP 100/35 A.D.=1.89 g/cc



100X 234-40B3

100X 234-40B1

Parallel to Axis Run 118-2 Perpendicular to Axis
RTP 90/10/32, A.D. = 1.95 g/cc

Figure 13. Photomicrographs of IPB Graphite - Aggregate R

TABLE 15

COEFFICIENT OF THERMAL EXPANSION, 0° to 75°C [3]

IPB[1] Run No.	Formulation	CTE, 10^{-7}/°C of IPB Graphite			Graphitized Extruded Rod	
		Axial	Diam.	A.R.[2]	Aggregate	CTE, 10^{-7}/°C
121-2	GP 100/35	35.7	18.7	1.91	G	13.7
107-2	GTP 75/25/27	30.7	22.1	1.39		
122-1	CP 100/32	28.6	18.4	1.56	C	16.2
110-1	CTP 75/25/21	32.8	24.6	1.33		
118-1	VP 100/32	48.0	--	--	V	38.0
116-1	VTP 75/25/25	49.0	44.2	1.11		
117-1	RP 100/35	40.5	36.5	1.11	R	32.2
118-2	RTP 90/10/32	42.9	41.4	1.02		
114-1	RTP 75/25/27	47.2	45.3	1.04		
117-2	SP 100/32	40.0	35.7	1.12	S	26.7

(1) All runs selected were made at standard IPB conditions.

(2) Anisotropy ratio, axial/diametral values.

(3) Properties listed are for specimens graphitized at 2500°C.

tends to decrease the anisotropy ratio and to increase the CTE (exception - axial CTE with aggregate G).

°C

4. CONVENTIONAL BAKING OF PREFORMS

Two or more cylindrical preforms were pressed from all of the mixes made in the course of the IPB program. To provide a basis for comparing the properties of the IPB graphite products with those obtainable by conventional processing, duplicate specimens of most of the IPB preforms were loaded into a sagger with granular graphite packing medium and baked to 1000°C on a standard 7 day schedule. Unfortunately, many of the specimens showed evidence of having been "overpressed" for conventional baking, i.e., laminar cracking and bloating prevalent. The scope of the program did not permit repeating the mixes and determining optimum molding pressures for each formulation.

These baked specimens which appeared to be relatively sound were graphitized (100°C/hr. to 2500°C) and tested. The properties of the graphite specimens are listed in Table 16. The properties are generally inferior to those of similar preforms subjected to standard IPB processing, especially with respect to density and permeability.

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TABLE 16

CONVENTIONAL BAKING[1] OF SPECIMENS SIMILAR TO IPB PREFORMS

Specimen No.	Formulation	Green (Preform) Density, g/cc	Properties of Graphitized (2500°C) Specimens						
			Apparent Density, g/cc	Permeability, 10^{-2} cm^2/sec		Flexural Strength, 10^3 psi		Compressive Strength, 10^3 psi	
				Axial	Radial	Axial	Diam.	Axial	Diam.
484-22D1	GP 100/35	1.79	1.58	470	700	0.65	0.99	2.96	3.14
-22H2	GTP 90/10/33	1.81	1.67	120	280	2.15	2.80	5.05	4.45
-22M1	GTP 85/15/34	1.81	1.72	54	110	2.06	2.95	5.57	4.78
-9B1	GTP 75/25/29	1.78	1.66	190	330	0.83	1.03	2.83	2.83
-9A1	GTP 75/25/27	1.76	1.59	370	860	0.53	0.65	2.08	2.07
-22C1	GTP 75/25/25	1.75	1.60	1100	1500	0.54	0.63	2.56	2.59
-1A5	GTP 75/25/23	1.77	1.52	340	1000	0.30	0.46	1.65	1.84
-22A1	GTP 75/25/21	1.71	1.51	430	690	0.74	1.08	3.78	4.26
484-22F1	CP 100/32	1.69	1.59	87	280	2.69	2.84	5.80	5.74
-22J2	CTP 90/10/30	1.74	1.64	75	130	2.66	2.77	6.53	5.86
-22P1	CTP 85/15/31	1.75	1.69	410	210	2.82	3.16	5.84	6.23
-9D1	CTP 75/25/24	1.73	1.76	65	120	1.55	2.14	5.08	4.89
-9C1	CTP 75/25/21	1.70	1.70	200	320	0.65	0.99	2.96	3.14
378-37B5	VP 100/32	1.65	1.77	170	420	3.35	4.21	9.98	8.91
-38B12	VTP 90/10/33	1.69	1.84	37	54	4.64	3.64	12.20	11.10
378-37B1	RP 100/35	1.65	1.71	1400	1200	1.94	2.62	6.42	5.64
-38B7	RTP 90/10/33	1.65	1.73	4900	3000	4.09	3.29	8.00	6.87
-38B13	RTP 85/15/31	1.65	1.80	1000	1700	4.06	3.65	9.31	8.26
378-37A3	SP 100/32	1.75	1.75	96	200	2.20	2.27	8.13	7.63

(1) Specimens 2-5/8 in. diam. x 5-1/4 in. long baked in saggers with granular packing medium to 1000°C in 7 days. Graphitized at rate of 100°C per hour to 2500°C.

5. COKING VALUE EXPERIMENTS

Previous experience and numerous literature references have indicated that the coke yield of binder pitch is increased by baking at elevated gas pressure. Run 128-1 (Table 4, section 3.1.3.) demonstrated that high coke yield resulting from high gas pressure alone (no isostatic mechanical pressure was applied) is not primarily responsible for the high graphite densities obtained in the IPB process.

Because of mechanical loss of pitch to the granular packing, it was not feasible to determine the binder coke yields in regular IPB runs. Since data on pitch coke yields at gas pressures as high as 1800 psig have not previously been reported (to the writer's knowledge), and equipment suitable for supplying such information was conveniently at hand, it seemed appropriate to make this contribution to the store of recorded knowledge.

Short molded specimens (2 5/8 in. diam. x 1 1/2 in.) from three different formulations used in the IPB program were placed in covered ointment tins and packed inside of the deformable metal containers in the IPB pressure vessels. Four runs were made at the 2-hour upheat to 590°C. In all runs the crossover valve between the internal and external pressure lines was left open. One run was made at atmospheric pressure, one at 900 psig, and one at 1800 psig. In the latter two the pressure was supplied by vapor pumped nitrogen from high pressure cylinders (National Cylinder Gas Company), added to the atmospheric pressure air which was in the system (this was the practice followed in all IPB runs). In the fourth run the system was evacuated three times and backfilled with nitrogen, then pressured to 1800 psig. All pressured runs were vented to atmospheric after the 2-hour upheat and held at 590°C for a total run time of 7 hours. All specimens were rebaked in a nitrogen atmosphere at 100°C/hr. to 1000°C in a graphite resistance tube graphitizer. The results are given in Table 17 along with coking values calculated from the same three formulations in the conventional baking run.

The very high pitch coke yield of 85% at 1800 psig nitrogen (ca. 0.17% concentration of oxygen) pressure approached the maximum theoretical yield possible (ca. 92% to 94% carbon plus other non-volatile constituents). The pitch coke yields at 900 psig nitrogen (ca. 0.33% oxygen) pressure and 1800 psig nitrogen (0.000% oxygen) pressure were slightly lower (83.8% and 83.5%, respectively). At atmospheric pressure the pitch coke yields were 68.0% for the fast bake, and 82.0% for the conventional bake.

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TABLE 17

COKING VALUE DETERMINATIONS AT VARIOUS GAS PRESSURES

Formulation	1000°C Coke Yield[1], % of Pitch Binder: Fast Bake[2], Some Oxygen in Environment[3] 0 psig	900 psig	1800 psig	Fast Bake[2], Pure Nitrogen Environment[4] 1800 psig	Slow Bake[5] 1800 psig
GP 100/35	67.6	86.6	86.0	85.9	77.6
GTP 75/25/27	67.8	83.9	84.9	82.5	68.9
CTP 75/25/24	68.5	81.0	84.1	82.2	69.4
Mean	68.0	83.8	85.0	83.5	72.0

(1) Calculated from weight loss at 1000°C, assuming no weight loss by aggregate.

(2) Baked in IPB apparatus, 2-hour upheat to 590°C, pressure vented to atmospheric pressure, held at 590°C for total run time of 7 hours. Rebaked at 100°c/hr to 1000°C.

(3) From air in system before pressurizing with N_2. Estimated O_2 concentration in void spaces at beginning of runs; 21% at 0 psig, 0.33% at 900 psig and 0.17% at 1800 psig.

(4) System evacuated and backfilled with nitrogen three times before pressurizing.

(5) Specimens similar to IPB preforms baked in sagger with packing medium on 7-day schedule to 1000°C.

6. DISCUSSION OF RESULTS

The substitution of isostatic pressure baking for the conventional baking step in the processing of mixtures of carbonaceous aggregate and coal tar pitch results in a graphitized product having high density and superior physical properties. This effect is obtained without impregnation or other post-treatment of the product. The IPB process is unique in that it consists of rapidly baking a preformed mixture under controlled gas pressure, with a controlled isostatic mechanical pressure superimposed on the body. This superimposed mechanical pressure is the result of a higher gas pressure external to a deformable metal container surrounding the body and granular packing medium.

While the coke yield of the pitch binder is increased significantly by the high gas pressure inside the container during upheat, this effect is not primarily responsible for the greatly increased graphite density obtained in the IPB process. A nominal differential, or isostatic mechanical, pressure is required during the relatively rapid upheat to maintain the structural integrity of the body. An increased isostatic mechanical pressure after the rapid upheat to 590°C (accomplished by decreasing the internal gas pressure) serves to consolidate the body to a higher density.

As the temperature reaches the range in which the more volatile constituents of the pitch normally distill from the body (i.e., in a conventional atmospheric pressure bake), the distillation is suppressed by the high vapor pressure..(1) Consequently, these constituents are exposed to a higher temperature than in a conventional bake, and due to participation in polymerization and pyrolysis reactions while still in the body are responsible for the increased coke yield.

This change in the distillation pattern of the pitch binder is also reflected in a changed rheology of the body. Data have been presented which demonstrate that, when heated rapidly, the body remains highly plastic at 590°C and 1800 psig gas pressure. A controlled release of the gas pressure results in a simultaneous increase in the isostatic mechanical pressure on the body, resulting from the 2200 psig pressure external to the deformable metal container in which the body is packed (in a granular packing medium). As further volatilization, polymerization, and cracking of the pitch progresses during the venting step, the

(1) From a thermodynamic standpoint, the assumption must be made that, under the conditions existing in the IPB process, the vapor phase in the pores of the body and in contact with its surface consists primarily of species identical with those in the liquid phase. This assumption requires that distillation is sufficiently rapid to prevent effectively the back diffusion of the indifferent gas (nitrogen) used to pressurize the system.

real volume and plasticity of the binder phase decreases. Thus, as increasing pressure is required to overcome the increasing rigidity of the body, it is automatically provided by the increasing isostatic mechanical pressure, and consolidation of the body to a higher density results.

After the internal gas pressure has been decreased to atmospheric pressure, the body still retains some degree of plasticity, as demonstrated by IPB runs with various holding times at 590°C.

The standard IPB process temperature of 590°C employed for the major portion of the program is very near the critical temperature for the venting step (release of internal gas pressure) and holding period at maximum isostatic mechanical pressure. An increase in process temperature to 620°C at a reduced external pressure (1800 psig - necessitated by safety considerations) resulted in no further increase in density or strength, although reproducibility of physical properties was apparently improved.

Extrapolation of data obtained with several process pressures at 590°C indicates that a significant gain in product density and other properties may be expected by an increase in pressure capability of the process.

The major share of the investigation of process variables of the IPB process was conducted with a graphite flour aggregate. Application of the optimum process conditions established in this way to four ungraphitized flour aggregates resulted in a number of graphite specimens having higher densities and strengths. The use of calcined Gilsonite coke flour resulted in graphite having a density of 1.92 g/cc, flexural strength in excess of 4,000 psi, and compressive strength in excess of 16,000 psi. Graphite produced using an isotropic aggregate previously developed under company sponsored research had an apparent density of 1.95 to 1.96 g/cc, and was essentially isotropic with respect to all physical properties. Flexural strength was in excess of 6,000 psi, and compressive strength was in excess of 14,000 psi.

7. RECOMMENDATIONS

The objective of this program was to investigate isostatic pressure baking of carbonaceous mixtures as a means of fabricating improved graphites. This objective was fulfilled within the scope of the program and the process capabilities of the equipment existing at the beginning of the program.

In view of the high graphite densities and strengths obtained in certain phases of the investigation, the following recommendations for further work on the IPB process are made:

(1) Obtain equipment with increased process capability with respect to temperature, pressure, and size of specimen accommodated. A preliminary study indicates that the most feasible type of equipment for meeting these requirements would be a cold wall pressure vessel with an internal furnace.

(2) Investigate more thoroughly the potential of isotropic aggregates and high softening point pitches. The process variables established as optimum for the graphitic aggregate and the standard coal tar pitch binder may not necessarily have been the optimum conditions for the other raw materials screened.

(3) Study the effects of particle size distribution of the aggregates on graphite properties. Also, an increase in particle size of the aggregates may be desirable with increased specimen size.

(4) Study the effects of various methods of preforming the carbonaceous mixtures on the isotropy of properties of graphite specimens produced by the IPB process.

(5) Produce IPB graphite specimens in sufficient size and quantity for testing in selected applications. For example, the high strength and low permeability of some specimens produced in the present program suggest resistance to high temperature erosion. The high isotropic CTE of some specimens suggests compatibility with certain protective coatings.

APPENDIX I

CHARACTERIZATION OF RAW MATERIALS

Designation	Identification and Source
G	Grade 1008 graphite flour, commercial, Great Lakes Carbon Corporation.
C	Grade 3002 calcined coke flour, commercial, Great Lakes Carbon Corporation.
V	Calcined Gilsonite coke flour, commercial, American Gilsonite Company.
R,S	Isotropic carbon aggregates, previously developed under company sponsored research.
T	Thermax, a thermal furnace black, commercial, Thermatomic Carbon Company.
P	No. 30 medium coal tar pitch, commercial, Allied Chemical Company.
O	High softening point coal tar pitch, previously developed under company sponsored research.
Q	Grade 350 industrial coal tar pitch, commercial, Allied Chemical Corporation.

	Coal Tar Pitch Binders		
	O	P	Q
Specific Gravity at 25°C	1.31	1.30	1.31
Softening Point (C/A), °C	169	100	178
Benzene Insoluble, %	32	30	48
Quinoline Insoluble, %	0.0	12	25
Coking Value, %(1)	77	72	33

(1) Four-hour upheat to 950°C in platinum crucibles.

APPENDIX I

(Cont.)

	Carbon Aggregates					
	G	C	V	R	S	T
Wet Seive Analysis,						
% Passing 100 Mesh	77.6	93.8	99.9	80.1	67.3	(1)
200	48.7	54.9	61.1	64.2	49.2	
400	28.4	26.1	39.4	28.7	37.4	
Total Ash, %	0.53	0.24	0.80	0.48	0.36	0.3
Real Density, g/cc	2.20	2.07	1.98	1.90	2.06	1.89
Coefficient of Thermal Expansion, $10^{-7}/°C$(2)	13.7	16.2	38.0	32.2	26.7	-

(1) Average particles size reported by supplier as 0.3 micron.

(2) Temperature range 0° to 75°C, extruded pitch bonded specimens.

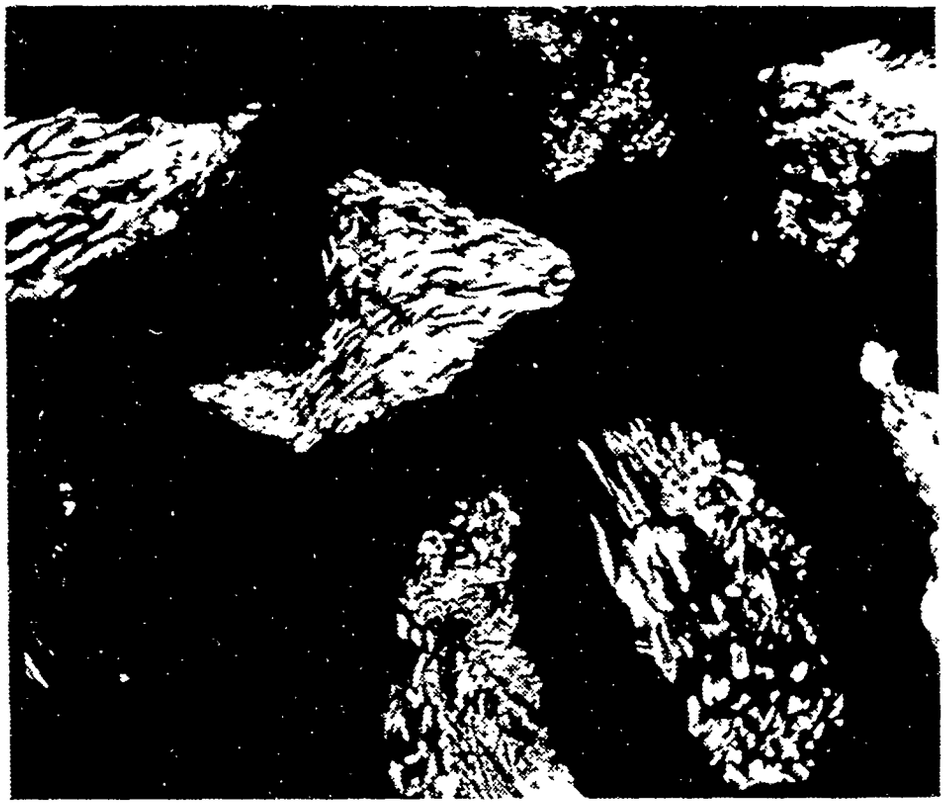
200X 234-38D1

Parallel Nicols

200X 234-38D2

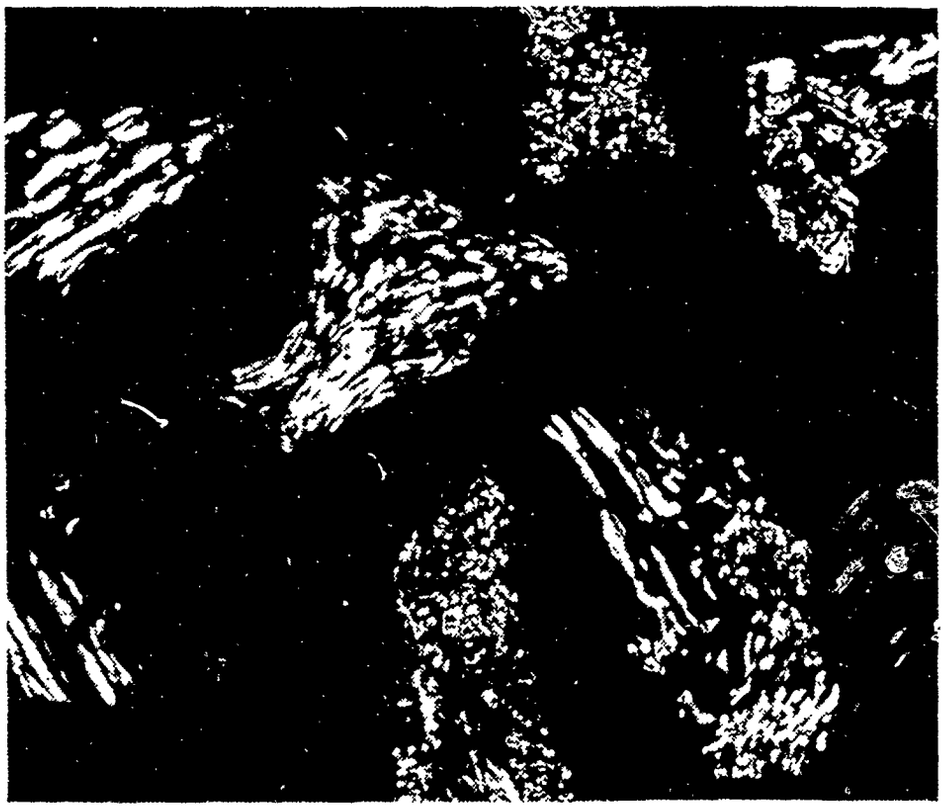
Crossed Nicols

Figure 14. Photomicrographs of Aggregate G (65/100 Mesh)



200X 234-38C3

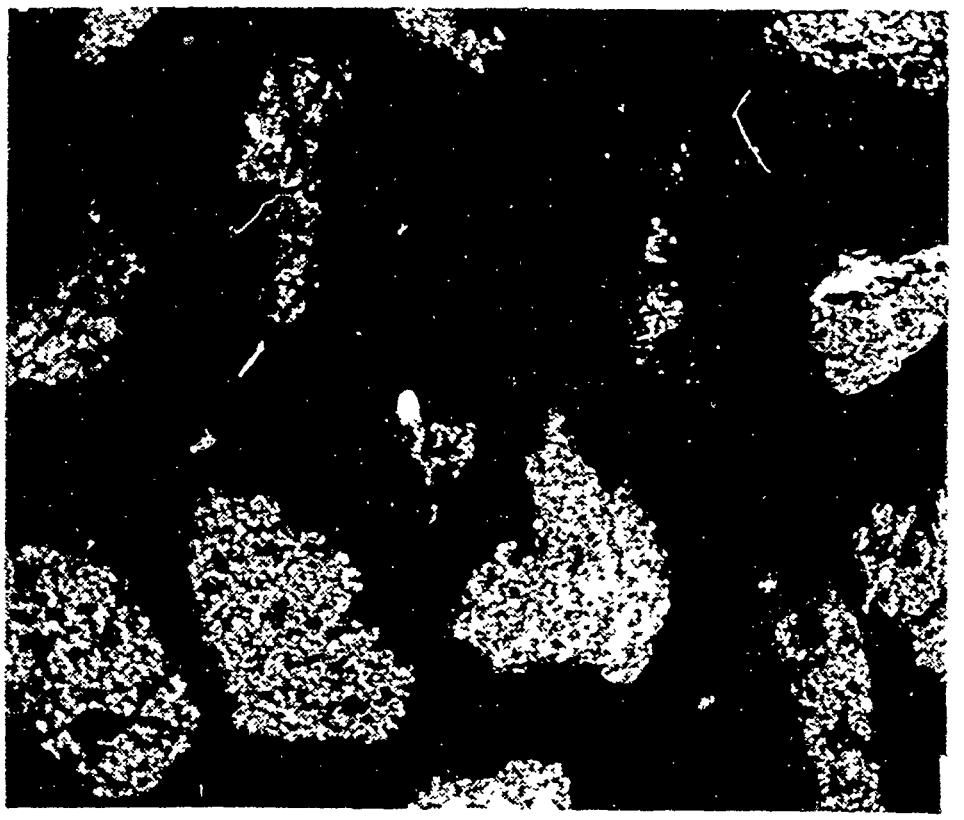
Parallel Nicols



200X 234-38C4

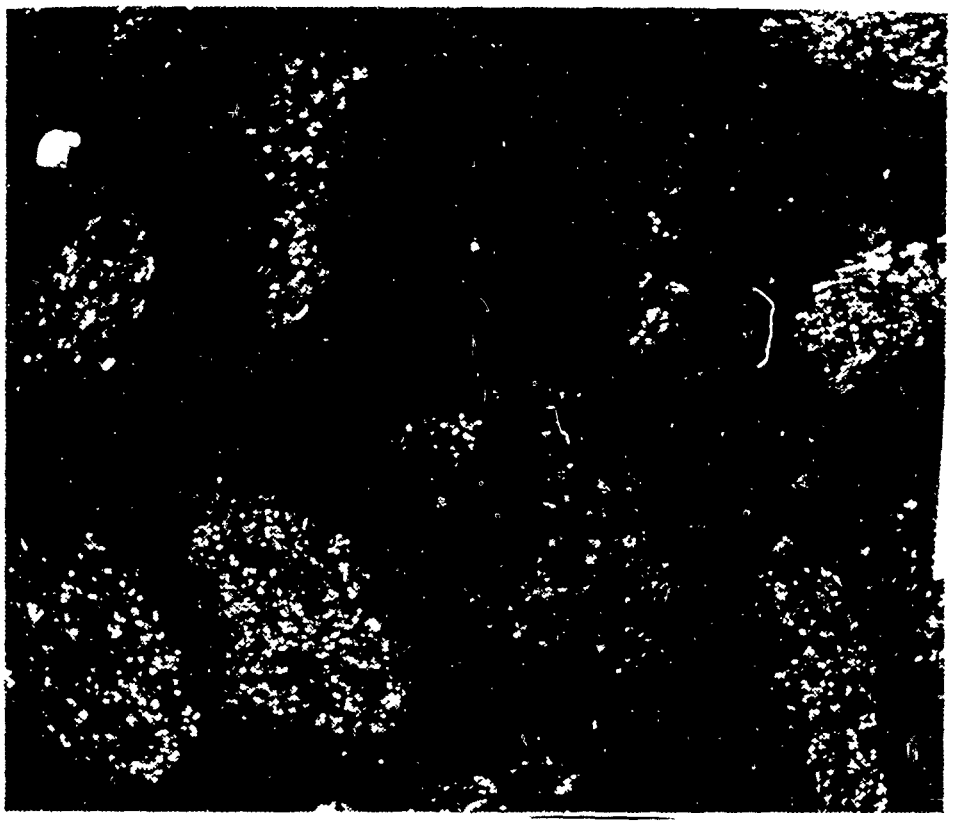
Crossed Nicols

Figure 15. Photomicrographs of Aggregate C (65/100 Mesh)



200X 234-38E5

Parallel Nicols



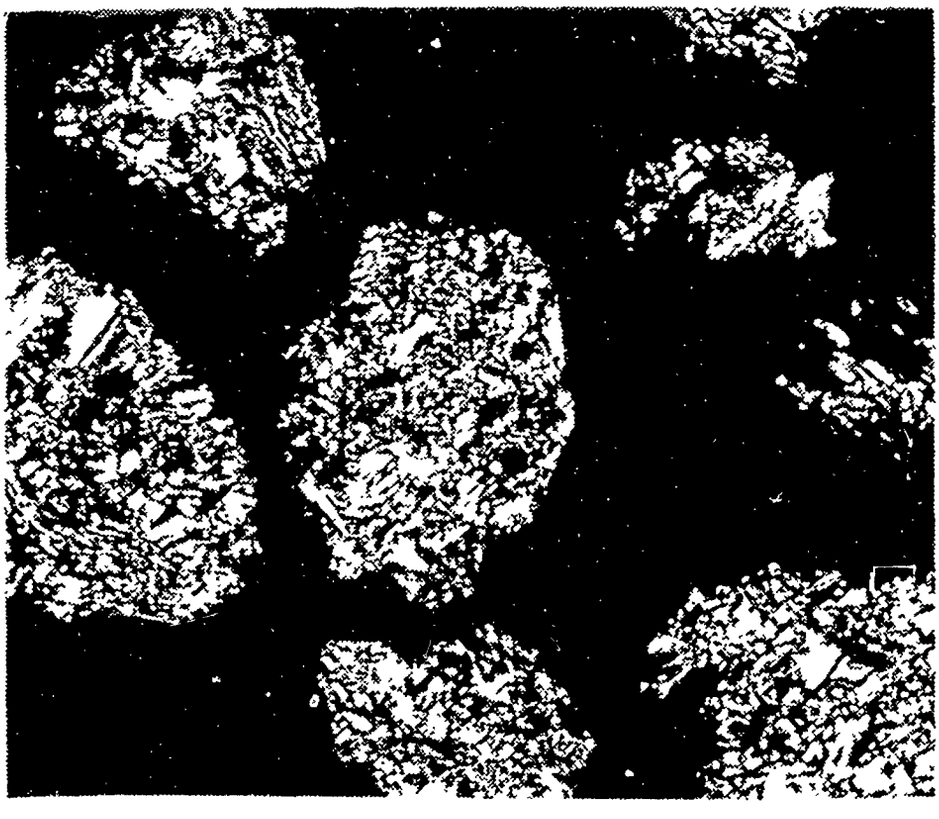
200X 234-38E6

Crossed Nicols

Figure 16. Photomicrographs of Aggregate V (65/100 Mesh)

200X 234-38A1

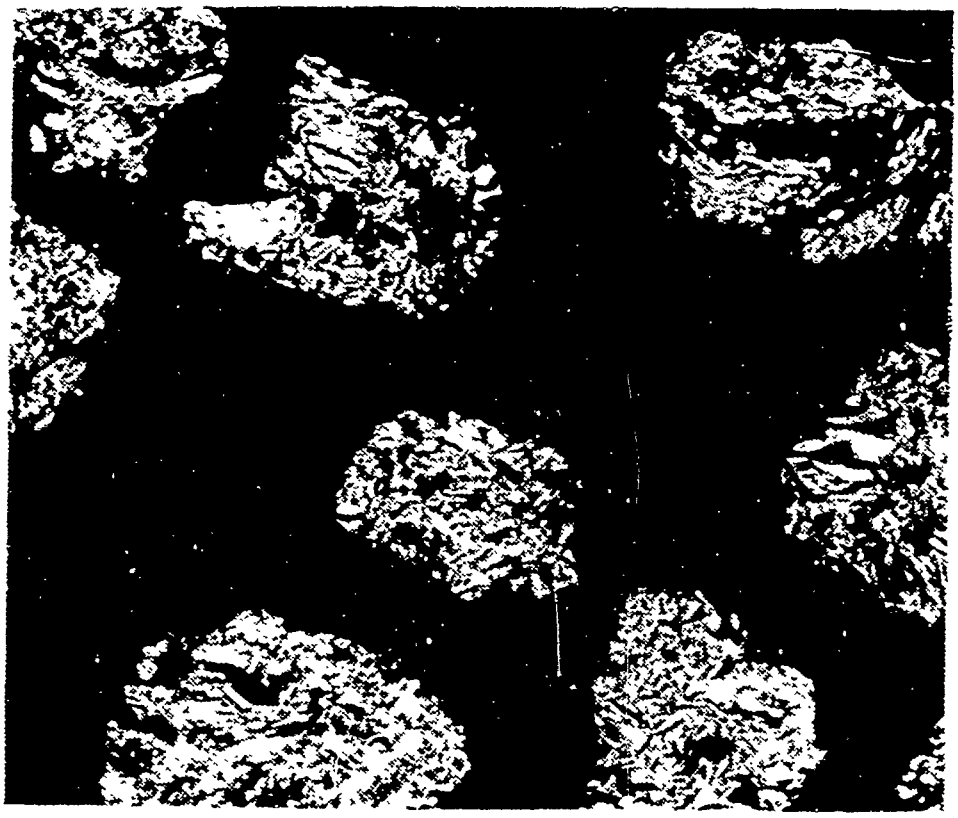
Parallel Nicols



200X 234-38A2

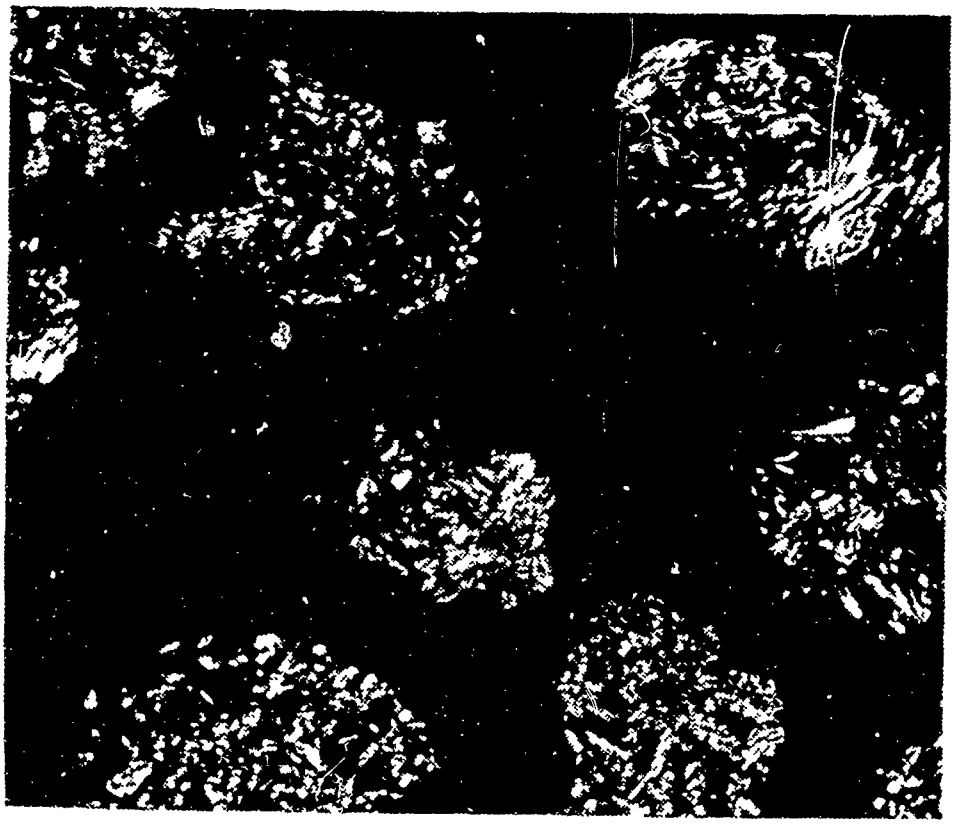
Crossed Nicols

Figure 17. Photomicrographs of Aggregate R (65/100 Mesh)



200X 234-38B3

Parallel Nicols



200X 234-38B4

Crossed Nicols

Figure 18. Photomicrographs of Aggregate S (65/100 Mesh)

APPENDIX II

TEST PROCEDURES

II.1. Apparent Density

Apparent volume of the green preforms was determined by measurement, and of the whole IPB and graphitized IPB specimens by weighing in a saturated condition in water and in air. Apparent volumes of all axial permeability specimens, and of a few flexural strength specimens were determined by measurement.

$$\text{Apparent Density, g/cc} = \frac{\text{Dry weight in air, g}}{\text{Apparent volume, cc}}$$

II.2. Permeability

A cylindrical specimen 2.0 in. diam. x 1.5 in. long was machined from near one end of the whole specimen. Axial permeability to helium gas was determined by clamping the solid cylinder in a 2.0 in. I.D. rubber hose attached to a metal container of known internal volume. After establishing a helium atmosphere in the container at a pressure in excess of 50 psig, the time required for pressure decay, by flow through the specimen, from 50 to 30 psig or from 45 to 35 psig was determined. Axial permeability was calculated according to the formula:

$$F = \frac{LV}{At} \ln \frac{G_o}{G}$$

where F = the permeation constant expressed in $cm^2/sec.$,
L = the axial length of the specimen, cm,
A = the cross-sectional area of the specimen, cm^2,
V = the internal volume of the system (container, lines, test gage), cm^3,
t = the time for pressure decay, sec.,
G_o = the initial gage pressure, any unit,
and G = the final gage pressure, same unit as G_o.

After determination of the axial permeability, a 0.500 in. diam. hole was drilled along the axis of the cylindrical specimen, which was then clamped between two metal plates with rubber cement in the interfaces. The bore of the hollow cylinder was connected to a system of known volume through one of the metal plates, and radial permeability was determined by observing the rate of helium pressure decay, as before. In this case:

L = the wall thickness of the hollow cylinder = 1/2 (D-d), cm,
D = the outside diameter of the cylinder, cm,

d = the inside diameter of the cylinder, cm,
h = the axial length, or height of the cylinder, cm,
A = the logarithmic mean area of the cylindrical wall, cm^2

$$A = \frac{\pi h\,(D-d)}{\ln \frac{D}{d}}$$

and V = the internal volume of the system, including the bore volume of the cylinder, cm^3.

The formula, $F = \frac{LV}{At} \ln \frac{G_o}{G}$ thus becomes

$$F = \frac{(D-d)V}{2\pi h(D-d)t} \ln \frac{D}{d} \ln \frac{G_o}{G}$$

$$F = \frac{V}{2\pi h\, t} \ln \frac{D}{d} \ln \frac{G_o}{G}$$

II.3. Flexural Strength

The remainder of the whole specimen was cut into three 0.50 inch thick slabs on planes parallel to the axis and to each other, with the center slab including the original axis. The cut surfaces were lapped smooth with a slurry of 600 mesh silicon carbide. Three square cross-section prisms (0.50 in. x 0.50 in. x ca. 2.25 in.) were cut from the center slab, with the long direction perpendicular to the original axis. Three similar prisms (0.50 in. x 0.50 in. x ca. 3.5 in.) were cut from the other slab or slabs, with the long direction parallel to the original axis. The sets of specimens were designated diametral and axial, respectively. After lapping the two new surfaces of each prism, washing, oven-drying, and cooling to room temperature, the prisms were loaded to failure in a flexural strength fixture mounted in a laboratory hydraulic press. The span was 2.00 in. and loading was at the center point. With both axial and diametral prisms, the load was applied in a direction perpendicular to the original axis. Flexural strength was calculated according to the formula:

$$F.S. = \frac{3\,W\,l}{2\,b\,d^2}$$

where F.S. = the flexural strength, psi ($lb./in^2$),
W = the load at failure, lb.,
l = the span between supports, in.,
b = the breadth (perpendicular to direction of loading), in.,
and d = the depth (parallel to direction of loading), in.

II.4. Compressive Strength

One end from each of the broken flexural strength specimens was then cut to produce a prism 0.50 in. x 0.50 in. x 1.00 in.,

and the ends were lapped smooth. After washing, oven drying, and cooling; each prism was loaded to failure while centered under a spherical bearing block in the laboratory press. Compressive strength was calculated according to the formula:

$$C.S. = \frac{W}{bd}$$

where C.S. = the compressive strength in psi,
W = the load at failure, lb.,
and b & d = the cross-sectional dimensions, in.

II.5. Electrical Resistivity

About half-way through the program, electrical resistivity was added to the list of routine physical tests. For this purpose, the flexural strength specimens were used before the flexural test. The specimens were clamped between two current leads from a Kelvin bridge, and carefully spaced (2.00 in.) potential probes were held in place while a direct current was passed through the specimen. Current density was chosen to avoid noticeable heating of the specimen in the time required to observe resistance values. Resistivity was calculated according to the formula:

$$E.R. = \frac{rA}{l}$$

where E.R. = the electrical resistivity, ohm in.,
r = the electrical resistance measured, ohm,
A = the cross-sectional area, in^2,
and l = the span between potential probes, in.

II.6. Modulus of Elasticity

At the same time resistivity measurements were begun, some of the axial flexural strength specimens were used, before flexural testing, for determination of modulus of elasticity in cantilever bending (the diametral specimens and some of the axial specimens were too short). One end of the specimen was clamped in a small machinist's vise, while incremental loads were applied 2.0 in. from the support through a guided rod ending in a spherical tip. Deflections were observed to 0.00005 in. precision by means of a dial indicator (0.0001 in. divisions) mounted beneath the specimen at the point of load application. The specimen was "exercised" by several applications of a load corresponding to ca. 40% of the estimated breaking load, then incremental loads were applied and deflections recorded. Straight line stress-strain curves were the rule, with the deflection returning essentially to zero on removal of load. Modulus of elasticity was

calculated according to the formula:

$$M.E. = \frac{4\ Wl^3}{f\ b\ d^3}$$

where M.E. = the modulus of elasticity (cantilever bending), psi,
W = the differential load, lb.,
l = the span between support and load, in.,
f = the differential deflection, in.,
b = the breadth (perpendicular to direction of loading), in.,
and d = the depth (parallel to direction of loading), in.